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16. ABSTRACT

An assessment of The Best Available Technology Economically Achievable (BATEA) for treatment of synthetic rubber manufacturing wastewaters has been conducted. This assessment was based on feasibility tests with actual wastewater samples, both end-of-pipe (untreated) and after primary and secondary treatment. The wastewater samples investigated were collected at representative facilities for manufacture of emulsion crumb, solution crumb and latex rubbers.

The physical-chemical treatment processes examined included dual-media depth filtration (DMDF) and ultrafiltration (UF) for suspended solids removal; activated carbon adsorption (ACA), reverse osmosis (RO) and ozonation for removal of dissolved contaminants; and ozonation as a polishing step after RO or ACA for removal of refractory organics. The proposed BATEA sequence of DMDF followed by ACA was examined for treatment of wastewater samples collected after secondary treatment. In addition, various combinations of the processes identified above were evaluated for both treatment of end-of-pipe effluents and secondary treated effluents.

Based on an assessment of process technical feasibility and estimates of wastewater treatment costs preferred options for control technologies were selected.

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ASSESSMENT OF BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE FOR SYNTHETIC RUBBER MANUFACTURING WASTEWATER

by

Myles H. Kleper
Arye Z. Gollan
Robert L. Goldsmith
Kenneth J. McNulty
Walden Division of Abcor, Inc.
Wilmington, Massachusetts 01887

Contract No. 68-03-2341

Project Officer

Ronald Turner
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Feasibility studies of the technical merit of various combinations of unit processes in treating synthetic rubber manufacturing wastewaters are discussed in this report. The proposed BATEA treatment scheme of dual-media depth filtration and activated carbon adsorption, and alternative advanced treatment processes (ultrafiltration, reverse osmosis, ozonation) were evaluated for treatment of emulsion crumb, solution crumb and latex manufacturing wastes. It is hoped that the results of this study will increase public and industry knowledge in this complex area and will promote interest in demonstration of the recommended treatment options at synthetic rubber manufacturing plants.

The Organic Chemicals and Products Branch of the Industrial Pollution Control Division should be contacted for further information on this subject.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

An assessment of The Best Available Technology Economically Achievable (BATEA) for treatment of synthetic rubber manufacturing wastewaters has been conducted. This assessment was based on feasibility tests with actual wastewater samples, both end-of-pipe (untreated) and after primary and secondary treatment. The wastewater samples investigated were collected at representative facilities for manufacture of emulsion crumb, solution crumb and latex rubbers.

The physical-chemical treatment processes examined included dual-media depth filtration (DMDF) and ultrafiltration (UF) for suspended solids removal; activated carbon adsorption (ACA), reverse osmosis (RO) and ozonation for removal of dissolved contaminants; and ozonation as a polishing step after RO or ACA for removal of refractory organics. The proposed BATEA sequence of DMDF followed by ACA was examined for treatment of wastewater samples collected after secondary treatment. In addition, various combinations of the processes identified above were evaluated for both treatment of end-of-pipe effluents and secondary treated effluents.

Based on an assessment of process technical feasibility and estimates of wastewater treatment costs the preferred options for control technologies are as follows:

Manufacturing Process	Preferred Control Technologies
Emulsion Crumb Rubber	1) Proposed BATEA sequence of DMDF and ACA for treatment of effluents from primary/secondary treatment.
Solution Crumb Rubber	1) For existing sources with primary/secondary treatment systems currently installed, the proposed BATEA sequence of DMDF and ACA.
	2) For new sources, an alternative to primary/secondary treatment followed by DMDF and ACA is treatment of end-of-pipe wastewaters by UF and RO, with possible water reuse.
Latex Rubber	1) Ultrafiltration for treatment of tank and tank car washdown streams (70-90% of wastewater flow), with treatment of UF product water and the remaining 10-30% of wastewater flow by biological treatment.

As these results are based on limited experimental data it is recommended that the conclusions from this assessment be confirmed by definitive field, pilot-scale demonstrations of the preferred control technologies.

This report was submitted in fulfillment of Contract No. 68-03-2341 by the Walden Division of Abcor, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from July 1, 1975, to October 1, 1976 and work was completed as of July 20, 1977.

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ENGLISH-METRIC CONVERSION TABLE

To Convert From	To	Multiply by
Inch	Meter	2.54×10^{-2}
Feet	Meter	3.05×10^{-1}
Square inch	Square meter	6.45×10^{-4}
Square Feet	Square meter	9.29×10^{-2}
Cubic Feet	Cubic meter	2.83×10^{-2}
Gallon	Cubic meter	3.79×10^{-3}
Pound	Kilogram	4.54×10^{-1}
Pound per sq. inch	Bar	6.89×10^{-2}
Horsepower	Watt	7.46×10^{2}
Gallon per day	Cubic meter per day	3.79×10^{-3}
Gallon per minute	Cubic meter per day	5.45
Gallon per sq. ft-day	Cubic meter per sq. meter-day	4.10×10^{-2}
Gallon per minute per sq. ft.	Cubic meter per sq. meter-day	5.87×10^{1}

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The original of this manuscript was prepared by Ms. Cheryl Renaud. Revisions to the text were made by Ms. Sharon Collins.

SECTION 1

INTRODUCTION

BACKGROUND

A high demand for natural rubber, coupled with its limited availability during the World War II era, led to the rapid development of the synthetic rubber industry in America. Government sponsored programs encouraged cooperation between synthetic rubber researchers in both background knowledge and production techniques from the early 1940's through the mid-1950's (1). This cooperative effort was highlighted by the production of GR-S type synthetic rubber in 1942. GR-S type rubber, now identified by its copolymers as styrene-butadiene rubber (SBR), has more than doubled in production since 1945. Today SBR production accounts for greater than 60% of the total U.S. synthetic rubber industry's yearly output (3). Current synthetic rubber production is approximately 3,000,000 metric tons/year (2) with seven major types of rubber being produced. Table 1 gives the main constituents, the percentage of the total market, and the projected growth rate for each of these synthetic rubbers.

Synthetic rubber production is based on the polymerization of selected monomers by either an emulsion (aqueous) or a solution (non-aqueous) route. In the emulsion process, colloidal-size droplets of monomer are polymerized in water to form a stable emulsion. The resulting suspension of colloidal rubber particles is chemically termed a high-polymer latex. Latex rubber is formed by removing excess monomer and adding antioxidants to the rubber suspension. Emulsion crumb rubber is produced by removing excess monomer from the suspension and coagulating it to form solid rubber particles ("crumb") which are then screened, washed, dried, and packaged. In solution polymerization, the monomers are dissolved in an appropriate solvent (e.g., hexane) and, in the presence of a catalyst, are polymerized to a thick rubbery solution called "cement". The cement is coagulated, dried, and packaged to form solution crumb rubber.

Synthetic latex and crumb rubber are being produced in over 30 plants within the U.S. with the major production sites located in the Texas/Louisiana Gulf Coast region and in Ohio. Current production is approximately 7% latex, 32% solution crumb and 61% emulsion crumb. Latex rubbers are widely used in paper, adhesive, and paint manufacture. The primary industrial uses of crumb rubber are in tire manufacture and automotive

TABLE 1. TYPES OF SYNTHETIC RUBBERS PRODUCED IN THE UNITED STATES

Synthetic Rubber Type	Monomer(s)	Process Type	Approximate Percentage of Total Synthetic Rubber Production	Typical Applications	Projected Growth Rate*
Butyl	Isobutylene Isoprene	Solution (crumb)	6%	Tires and tire products	2%- 6%
EPDM	Ethylene Propylene	Solution (crumb)	7%	Automotive parts, tires, wire insulation	5%-15%
Neoprene	Chloroprene	Emulsion (crumb)	7%	Automotive industry, aerospace and consumer products	0%- 4%
Nitrile (NBR)	Acrylonitrile Butadiene	Emulsion (70% crumb, 30% latex)	5%	Automotive and mechanical applications needing oil and solvent resistant rubber	3%- 7%
Polybutadiene	Butadiene	90% Solution (crumb), 10% Emulsion (crumb)	12%-15%	Truck, bus and passenger car tires	3%- 5%
Polyisoprene	Isoprene	Solution (95% crumb, 5% Latex)	5%	Tires	5%- 8%
Styrene-Butadiene (SBR)	Styrene Butadiene	90% Emulsion (90% crumb, 10% Latex) 10% Solution	55%-60%	Tires, mechanical goods	0%- 3%

*From reference (3), projected for 5 years beginning 1972.

accessories. Rubber produced by the solution polymerization process is generally more expensive than emulsion crumb rubber, but it is gaining in commercial applications since it exhibits higher abrasion and crack resistance than the emulsion type (3).

WASTEWATER LOADINGS OF MAJOR POLLUTANT PARAMETERS

The synthetic rubber industry, as a whole, discharges approximately 58 billion gallons of wastewater annually (2). Wastewaters from several synthetic rubber manufacturing facilities have been sampled and the major pollutant parameters determined (4). The point source loadings were categorized by process type - emulsion crumb, solution crumb, and latex - rather than by the type of rubber being produced. Although emulsion polymerization is used to produce both latex and emulsion crumb rubbers, the differences in the nature of the products, the nature of the wastes generated, and the treatability of the wastes are sufficient to warrant separate wastewater characterizations.

The main pollutant parameters were identified (4) to be chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids, and oil and grease. The median values obtained for these parameters are given in Table 2 for each process type. COD is the largest contributor to the pollutant load for all three process wastewaters.

SYNTHETIC RUBBER MANUFACTURING PROCESSES AND WASTEWATER CHARACTERISTICS

Emulsion Crumb

Emulsion polymerization followed by coagulation of the suspended polymer is the traditional, and most widely employed process for synthetic rubber production. A flow schematic of the emulsion crumb manufacturing process is given in Figure 1. Several production lines are employed simultaneously at manufacturing sites; however, for simplification, only one process train is shown in Figure 1. Emulsion crumb rubber production is a continuous operation with facilities typically operating 24 hours per day, 365 days per year.

Soaps, monomers, oil emulsions, stabilizers and specialty additives are kept in storage and used as required. There is no significant continuous wastewater discharge from the storage area. Wastewaters are, however, generated during intermittent cleaning or may result from accidental leaks. If necessary, water used in the preparation of raw solutions is deionized prior to usage. Softener regeneration is accomplished with a strong brine solution which results in a wastewater with a high dissolved solids concentration. A caustic soda scrub solution is used to remove inhibitor (e.g., terbutyl catechol) added to certain monomers (e.g., butadiene) to prevent premature polymerization during storage. The spent scrub waters are high in COD, pH, alkalinity and color; however, their flowrate is extremely low. In many plants, the spent scrub solution

TABLE 2. MEDIAN VALUES OF RAW WASTE LOADINGS FOR SYNTHETIC RUBBER MANUFACTURING PLANTS[*]

Process Type	Number of Waste streams Sampled	Average Wastewater Flowrate (m^3/metric ton)	COD kg/metric ton	BOD kg/metric ton	Suspended Solids kg/metric ton	Oil kg/metric ton
Emulsion Crumb[†]	6	16.6	19.63	2.56	6.64[††]	1.5
Solution Crumb	8	15.9	9.03	1.13	2.81[††]	1.08
Latex	2	13.5	34.95	5.31	6.17	0.33

[*] Table derived from information in reference (4).

[†] Includes utility wastewaters.

[††] Raw waste load determined downstream of crumb pits, where suspended solids and oil levels are reduced.

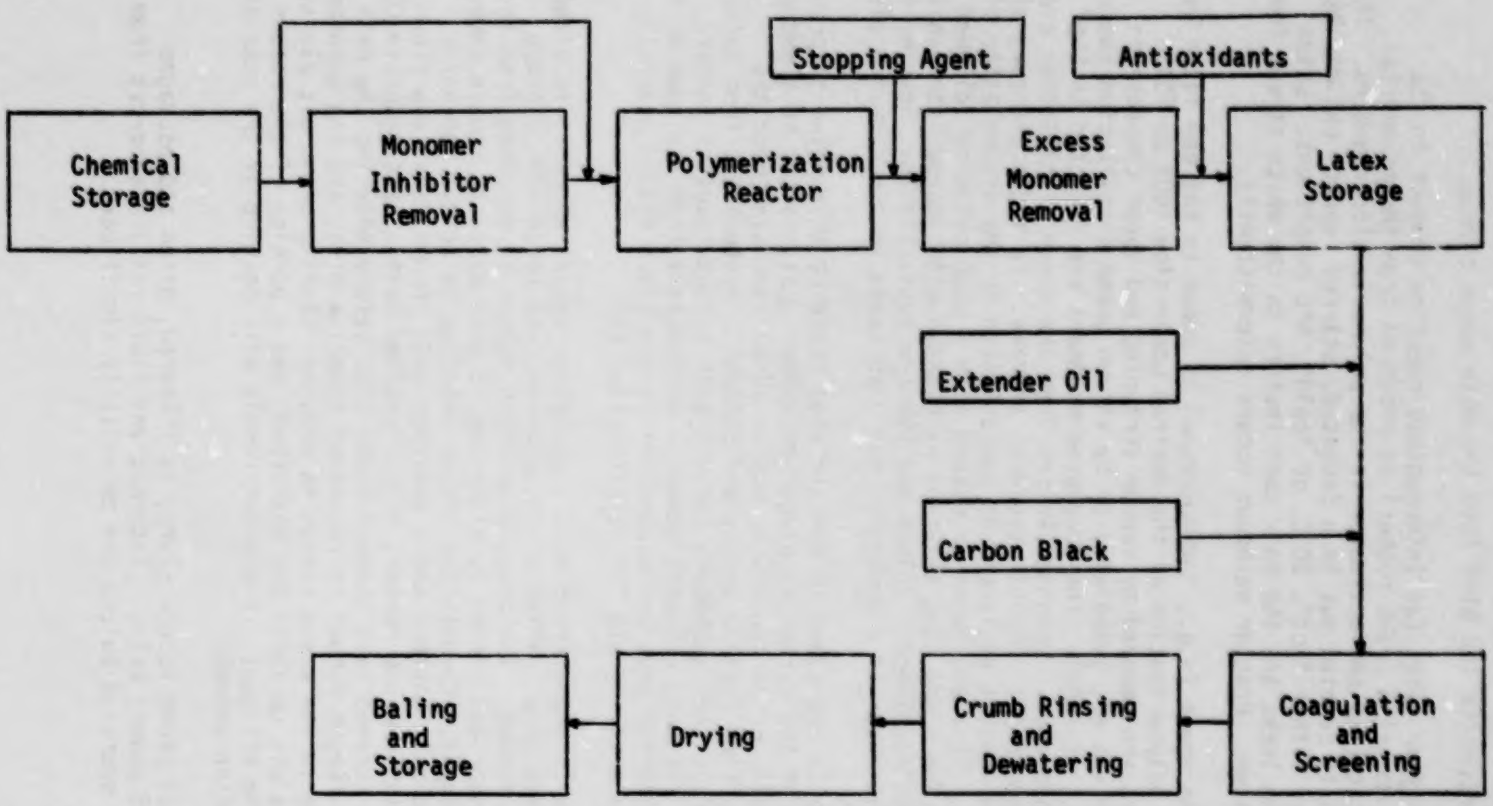


Figure 1. Simplified flow diagram of emulsion crumb rubber production.

is collected batchwise and bled into the main waste stream.

A high-polymer latex (an intermediate reaction product in the production of emulsion crumb rubber) is produced from the monomer(s), emulsifiers, catalyst and activator in the polymerization reactors. The polymerization is carried out in a jacketed, stirred reactor and may be performed under either "hot", 50°C, or "cold", 5°C conditions. Latex spills and pump leaks are the main contributors to the waste stream from this process step. Reactor washdown occurs intermittently.

A stopping agent (e.g., hydroquinone) is added to the raw latex to terminate the polymerization at the desired conversion (60% to 70%). Excess monomers are removed by vacuum stripping and vapor compression (light monomer - e.g., butadiene) or by vacuum steam distillation (heavy monomer - e.g., styrene). The recovered monomers are recycled to the chemical storage area. Decanter waters from the steam distillation are re-stripped to remove all possible residual styrene. Periodic cleaning of the excess monomer removal equipment is necessitated by the accumulation of rubber solids. This equipment is washed with a soap solution followed by a water rinse. The spent soap solution is blended with stored latex while the rinse water is discharged. Volume and COD are typically low, however high COD loading can occur if a pocket of occluded latex ruptures during cleaning.

Antioxidants are added to the stripped latex at this point to prevent deterioration of the rubber by oxygen or ozone. Latices may be blended together and oil, or carbon black, may be added depending upon the physical properties desired in the end product. Wastewaters from latex blend and storage tank washdowns contain high solids loadings and are discharged to the main effluent stream. Wastewaters from washdown of the carbon black storage area and cleanup of carbon black spills generally pass through a settling pit for clarification (4).

The latex is transferred to a coagulation vessel where it is mixed (typically) with an acidified brine solution, and large porous crumb particles are formed. The coagulated crumb rubber is screened from the coagulated liquor and rinsed by slurrying it with water to remove excess coagulation liquor. Coagulation liquor overflow is acidic and has a high dissolved salt content and a moderate COD. Crumb rinse overflow contains floatable crumb rubber, high dissolved solids, and moderate COD. Both overflow streams pass through crumb pits before entering the main flow channel. Crumb rubber is recovered from the pits, and the suspended solids loading in the waste stream is reduced. During crumb pit cleaning operations the pit contents are disturbed, and a portion of the rubber fines enter the effluent. A similar result will develop if the pits are not cleaned often enough.

The rinsed crumb rubber slurry is filtered, dried and packaged into 34 Kg (75 pound) bales. Intermittent fluid (oil) discharges from hydraulically operated balers are potentially significant.

Only 5% to 10% of the total wastewater flow for an emulsion crumb plant comes from the storage, polymerization, and stripping operations. The remaining 90% to 95% of the wastewater is contributed by the coagulation/rinsing/drying processes.

A summary of the wastewaters generated during emulsion crumb rubber manufacture has been developed (4) and is presented in Table 3.

Solution Crumb

Production of synthetic rubbers by solution polymerization with stereospecific catalysts has made it possible to consistently obtain the cis structure of the polymer (up to 98%) (11). This structure is characteristic of natural rubber and is physically more "rubbery" than the trans configuration. (Based on butadiene content, 65% to 72% of emulsion polymerized SBR molecules have the trans microstructure (1).) Solution crumb rubbers are therefore more stress and crack resistant than emulsion crumb rubbers, and they are beginning to partially replace emulsion SBR in tire manufacture.

A simplified flow schematic of the solution crumb rubber manufacturing process is shown in Figure 2. Those process steps which are identical to the emulsion polymerization process (i.e., produce similar waste streams) will not be discussed in detail. In a number of plants, solution and emulsion polymerized rubber are produced in parallel operations. Solution crumb plants typically operate 24 hours per day, year round.

Monomers, solvent (e.g., hexane, heptane, methyl chloride), and additive chemicals are held in storage tanks. Monomers are scrubbed with caustic soda to remove inhibitors, and both monomers and solvent are freed of water by passage through fractionator drying columns. The bottoms contain moderate COD and are discharged. Extraneous components present in the solvent recycle stream are also removed. These slop oils are containerized and may be used as a waste fuel.

The dried monomer and solvent streams are charged to the first of a series of reactors. A catalyst is introduced and a highly exothermic reaction is initiated. The reaction product is a highly viscous rubber "cement" containing about 25% solids. The polymerization is terminated by the addition of a "shortstop" solution, and the cement is pumped to holding tanks where antioxidants are added. Since the polymerization step must remain non-aqueous, the reactors are not washed down with water. A separately stored solvent solution is used whenever cleaning is necessary.

From the holding tanks the cement is transferred to coagulation vessels. "Extender" oil may be added during the transfer, and carbon black may be added during the coagulation step if the special properties imparted by these additives are desired. Surfactants are generally introduced into the coagulation vessels to control crumb size.

TABLE 3. SUMMARY OF POTENTIAL PROCESS-ASSOCIATED WASTEWATER SOURCES FROM EMULSION CRUMB RUBBER PRODUCTION[*]

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spend caustic Solution	High pH, alkalinity, and color. Extremely low average flow rate.
Monomer Recovery	Decant water layer	Dissolved and separable organics.
Coagulation	Coagulation liquor overflow	Acidity, dissolved organics, suspended and high dissolved solids, and color.
Crumb Dewatering	Crumb rinse water overflow	Dissolved organics, and suspended and dissolved solids.
Monomer Strippers	Stripper cleanout rinse water[†]	Dissolved organics, and suspended and dissolved solids. Possibly high quantities of uncoagulated latex.
Tanks and Reactors	Cleanout rinse water[†]	Dissolved organics, and suspended and dissolved solids. Possibly high quantities of uncoagulated latex.
All Plant Areas	Area washdowns	Dissolved and separable organics, and suspended and dissolved solids.

[*] Summary derived from Reference (4) with modifications.

[†] First rinse with soap solution which is discharged to finishing buildings and blended with latex. Second rinse with water, which removes soap residue, is discharged.

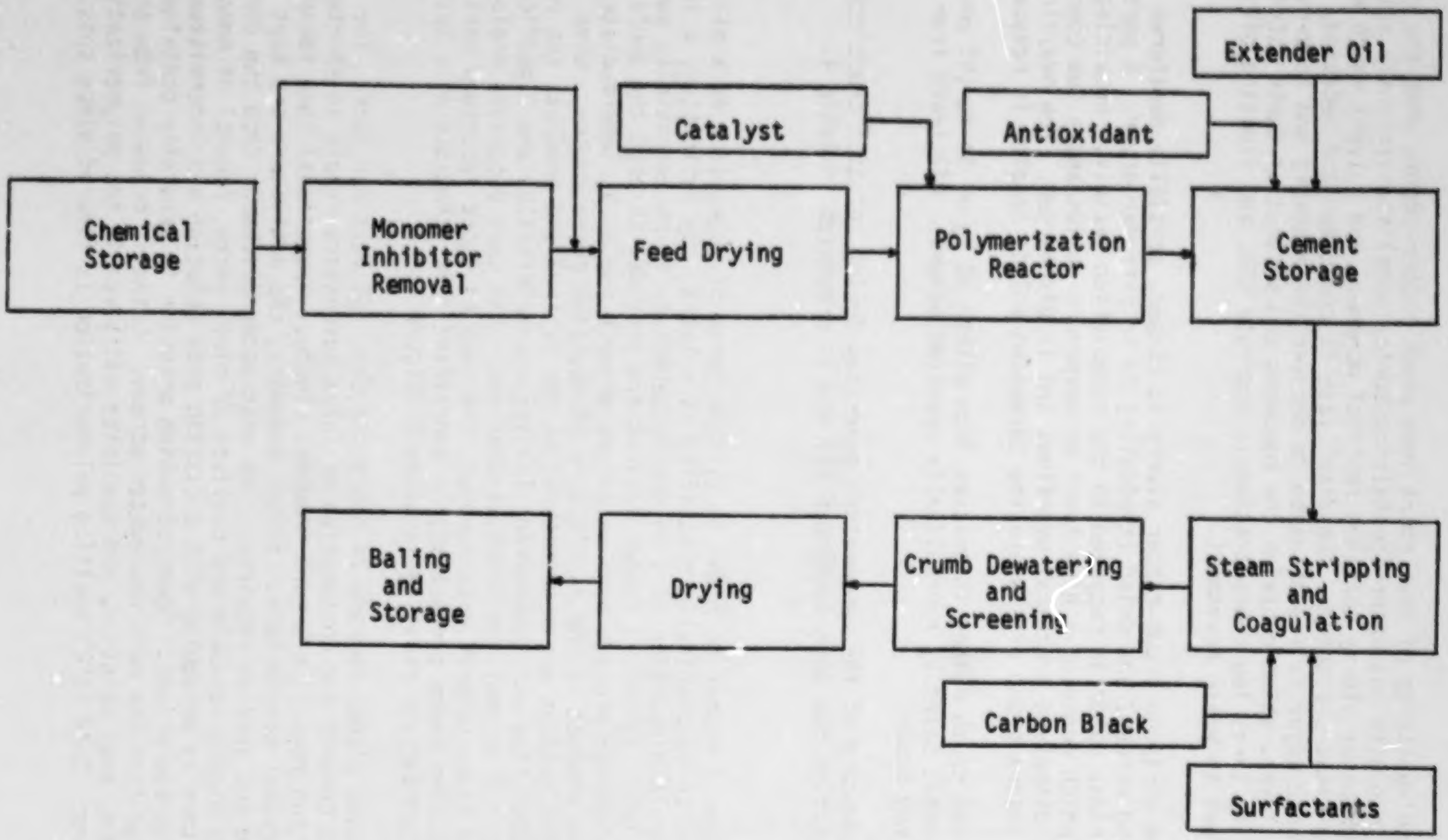


Figure 2. Simplified flow diagram of solution crumb rubber production.

Desolventizing of the cement into crumb rubber occurs when the cement is combined with hot water (containing surfactants) and violently agitated. The crumb/water slurry contains residual monomers and solvent which are removed by steam stripping. The distillate is condensed and decanted, and the organic layer is fractionated to recover the monomers and solvent. The aqueous layer, which contains the monomers and solvent at their saturation solubility (very low concentrations), moderate COD, and floating oils, is discharged to waste treatment.

The stripped crumb-rubber slurry is rinsed, partially dewatered by a vibrating screen, and dried (typically) in an extruder dryer. A portion of the rinse water is recycled to the coagulation vessels. Remaining rinse water, which contains a high level of suspended solids and a low concentration of dissolved organics, overflows and is discharged. The overflow stream enters crumb pits where the suspended solids loading is reduced.

Dried crumb rubber is pressed into either 23 Kg or 34 Kg (50 pound or 75 pound) bales by hydraulically operated balers. Oil leaks from the balers may occur.

A summary of the wastewaters generated during solution crumb rubber manufacturing has been developed (4) and is presented in Table 4.

Latex

Natural rubber is found in various forms of vegetation as a milky fluid which is chemically classified as a latex. By definition, a latex is a stable dispersion of a polymeric substance in an essentially aqueous medium (9). Synthetic rubber latices are produced through the emulsion polymerization process both as an end product and as an intermediate reaction product in the manufacture of emulsion crumb rubber. When synthetic latices are manufactured as the desired end product, the resulting wastewater flow and contaminant loading characteristics are significantly different from emulsion crumb wastewaters. The unit processes employed to produce latex rubbers are, however, the same as those described earlier for emulsion crumb production. A simplified flow schematic of a latex rubber production facility is given in Figure 3.

Latex plants operate 24 hours per day, 365 days per year. The varying product demands and consumption of latex purchasers result in shorter production runs (i.e., more frequent cleanout operations) than found in crumb rubber manufacture. Soaps, monomers, and activators are kept in storage and used as required. The wastewater discharge from the storage area is highly variable and consists of minor leaks, removal of monomer inhibitors by scrubbing with a caustic soda solution and intermittent cleaning operations. Spent scrubbing solution is generally containerized and bled into the main wastewater stream. Latex is produced from the monomers, soap solution, and specialty additives in the polymerization reactors. Cold (5°C) emulsion polymerization is favored since this results

TABLE 4. SUMMARY OF POTENTIAL PROCESS-ASSOCIATED WASTEWATER SOURCES FROM SOLUTION CRUMB RUBBER PRODUCTION (4)

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spent caustic solution	High pH, alkalinity, and color. Extremely low average flow rate.
Solvent Purification	Fractionator bottoms	Dissolved and separable organics.
Monomer Recovery	Decant water layer	Dissolved and separable organics.
Crumb Dewatering	Crumb rinse water overflow	Dissolved organics, and suspended and dissolved solids.
All Plant Areas	Area washdowns	Dissolved and separable organics, and suspended and dissolved solids.

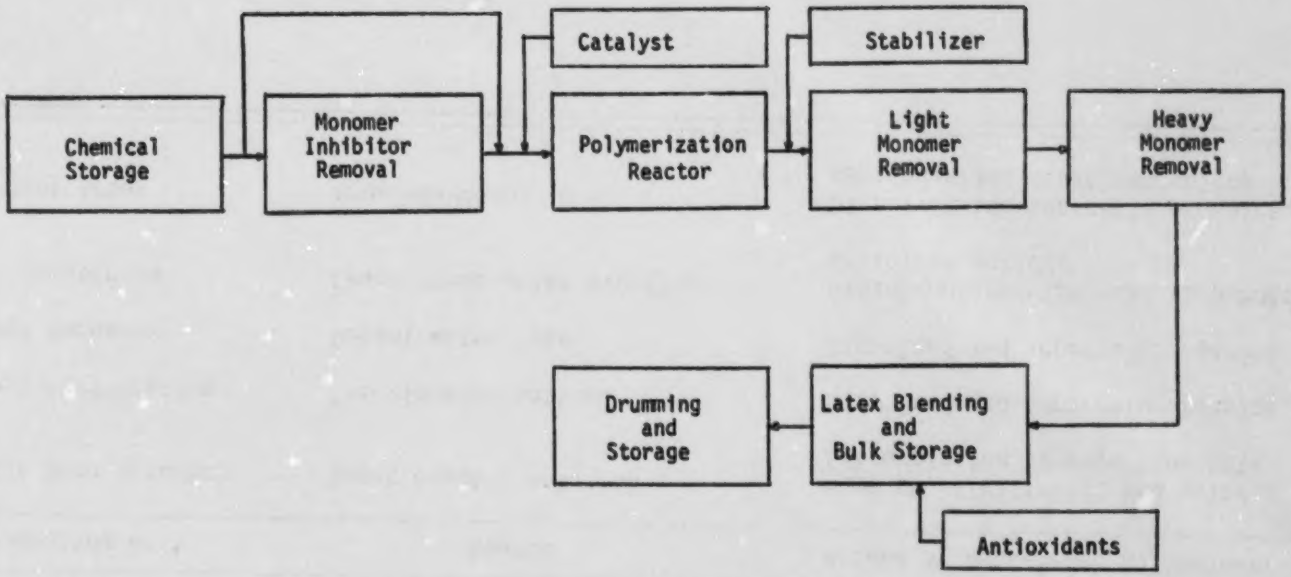


Figure 3. Simplified flow diagram of latex rubber production.

in better "packing" of molecules than under hot conditions and allows for a higher percentage of solids in the latex. Latex spills, pump leaks, and equipment cleanups are the main contributors to the waste stream flow from the polymerization step. The polymerizations proceed to ~98% conversion (as compared to ~60% conversion during emulsion crumb production). Excess monomers are removed by vacuum distillation (light monomer) and steam stripping (heavy monomer). Because of their limited volumes, it is not economically attractive to recycle the excess monomers after removal. The stripped heavy monomer and steam are condensed. The condenser bottoms are discharged and recovered heavy monomer is drummed for disposal. The decanter water contains both dissolved and separable organics. Stripped light monomer is flared then vented to the atmosphere.

After excess monomers have been removed, coagulated rubber solids are screened from the latex. The latex is then blended with antioxidants, stored in bulk, and shipped in 0.2 m^3 (55 gal) drum lots or via tank car. Both storage tank and tank car washdowns enter the main wastewater discharge stream. The washdown waters contain high COD, suspended solids, and uncoagulated latex and account for 70% to 90% of the total wastewater flow from a latex manufacturing plant.

A summary of latex process wastewaters and their characteristics is presented in Table 5 (4).

PROPOSED EFFLUENT LIMITATION GUIDELINES AND CURRENT TREATMENT PRACTICES FOR SYNTHETIC RUBBER MANUFACTURING WASTES

The Environmental Protection Agency has proposed effluent limitation guidelines and new source performance standards for the synthetic rubber industry based on both current waste treatment practices and economically achievable tertiary wastewater treatment. Table 6 details the proposed effluent guidelines. "Best Practicable Control Technology Currently Available" (BPCTCA) is defined as primary clarification to remove suspended solids followed by biological oxidation to remove oxidizable dissolved contaminants. The Federal Water Pollution Control Act requires that the BPCTCA guidelines by met by no later than 1 July 1977. "Best Available Technology Economically Achievable" (BATEA) is currently defined as primary and secondary treatment as in BPCTCA followed by dual-media depth filtration and activated carbon treatment to further reduce suspended solids and dissolved organic contaminants. The BATEA guidelines are to be met by 1 July 1983.

BPCTCA has been successfully demonstrated for synthetic rubber wastes (5), and it is currently in full-scale use at several synthetic rubber manufacturing plants (4). The data from these plants formed the basis for the development of the BPCTCA guidelines (4). The proposed BATEA guidelines are based on unpublished carbon adsorption studies conducted by the EPA, published literature, permit to discharge applications, and industry consultation and historical data (4).

TABLE 5. SUMMARY OF POTENTIAL PROCESS-ASSOCIATED WASTEWATER SOURCES FROM LATEX PRODUCTION (4)

Processing Unit	Source	Nature of Wastewater Contaminants
Caustic Soda Scrubber	Spent caustic solution	High pH, alkalinity, and color. Extremely low average flow rate.
Excess Monomer Stripping	Decant water layer	Dissolved and separable organics.
Tanks, Reactors, and Strippers	Cleanout rinse water	Dissolved organics, suspended and dissolved solids. High quantities of uncoagulated latex.
Tank Cars and Tank Trucks	Cleanout rinse water	Dissolved organics, suspended and dissolved solids. High quantities of uncoagulated latex.
All Plant Areas	Area washdowns	Dissolved and separable organics, and suspended and dissolved solids.

TABLE 6. PROPOSED EFFLUENT GUIDELINES FOR SYNTHETIC RUBBER INDUSTRY*,†

	Best Practicable Control Technology Currently Available						Best Available Technology Economically Achievable					
	Emulsion Crumb**		Solution Crumb**		Latex Rubber††		Emulsion Crumb**		Solution Crumb**		Latex Rubber††	
Constituent	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)	Limit (kg/metric ton)	Approx Conc. (mg/ℓ)
COD	8.00	500	3.92	245	6.85	500	2.08	130	2.08	130	1.78	130
BOD_5	0.40	25	0.40	25	0.34	25	0.08	5	0.08	5	0.07	5
Total Suspended Solids	0.65	40	0.65	40	0.55	40	0.16	10	0.16	10	0.14	10
Oil and Grease	0.16	10	0.16	10	0.14	10	0.08	5	0.08	5	0.07	5
pH	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9	6-9

* Proposed guideline published in Federal Register, Volume 39, Number 36, Thursday, February 21, 1974.

† Figures given are "30 day averages". These are lower than the daily maximum allowable discharge.

** Based on an average effluent flow rate of 3.3 m^3/metric ton of product.

†† Based on an average effluent flow rate of 2.83 m^3/metric ton of product.

A generalized flow schematic for primary and secondary treatment of synthetic rubber waste is shown in Figure 4 (4). The equalization basin provides a 24 hour residence time to smooth out flow and concentration variations. The basin is aerated to insure good mixing and prevent anaerobic conditions. The waste is then pH adjusted to about 7 which is optimum for both chemical coagulation and subsequent biological oxidation. Nutrients are also added to sustain microorganism growth in secondary treatment.

Wastes from emulsion polymerization processes (emulsion crumb and latex) may contain significant quantities of uncoagulated latex. These wastes are chemically coagulated in a reactor-clarifier using alum and polyelectrolyte as coagulants and finely divided clay or limestone as a sinker. Alternatively, chemical coagulation followed by air flotation removal of solids can be used (5) to achieve primary treatment. Coagulation and clarification are not required for solution crumb wastes since they do not contain waste latex.

Biological oxidation of the primary effluent is carried out in an aerated lagoon or an activated sludge plant. Microorganisms convert certain dissolved organics into insoluble biological solids reducing the BOD and COD of the waste. The effluent from biological treatment is clarified to remove biological solids before discharge from the plant.

Sludge from the secondary clarifier is partially recycled. The remainder is thickened and treated in an aerobic digester to reduce the bio-solid bulk. The sludge is then combined with sludge from the primary clarifier (for emulsion crumb and latex wastes), thickened, vacuum filtered, and hauled away for landfill.

To the best of the authors' knowledge, there are no full-scale BATEA systems currently in operation.

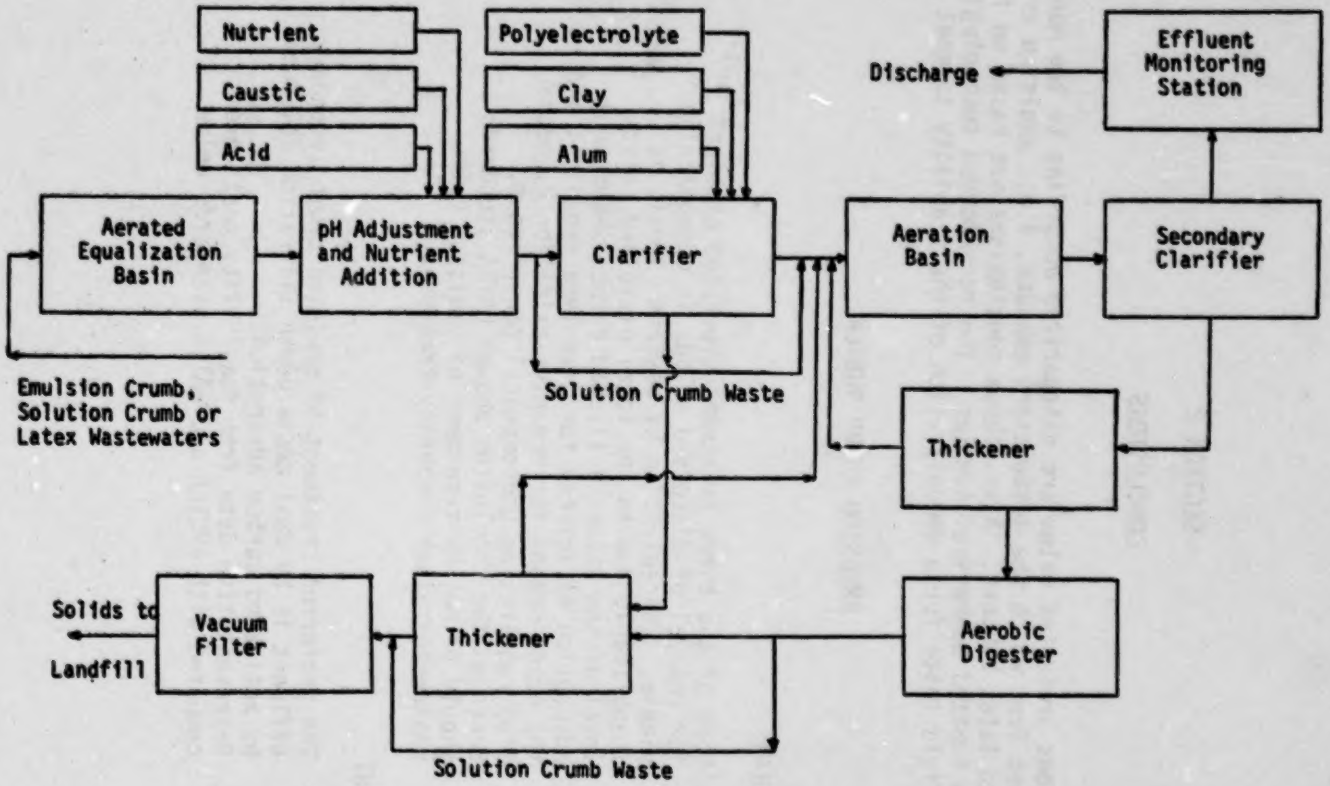


Figure 4. Simplified flow diagram of end-of-pipe secondary wastewater treatment facility for synthetic rubber manufacturing plant (4).

SECTION 2

CONCLUSIONS

The conclusions presented below are categorized according to the manufacturing processes from which the wastewaters emanate, i.e., emulsion crumb, solution crumb and latex rubbers. Also, these conclusions are based on feasibility tests with limited numbers of samples. The recommended technologies require on-site field tests for a demonstration of their ability to meet BATEA standards.

EMULSION CRUMB RUBBER

END-OF-PIPE EFFLUENT

1. None of the three treatment processes examined for removal of dissolved solids is economically viable. Concentration by reverse osmosis is inapplicable due to the total dissolved solids level of the waste; activated carbon shows poor adsorption efficiency for dissolved organics; and the ozone demand for organics oxidation by ozonation requires an uneconomical power input.
2. Based on the conclusion above, BATEA standards should be met by treatment of emulsion crumb wastewater after secondary treatment.

SECONDARY EFFLUENT

1. The preferred treatment of emulsion crumb secondary effluent is by dual-media depth filtration followed by activated carbon adsorption.
2. Representative data from feasibility tests are compared with BPCTCA and BATEA standards below:

Contaminant	Dual-Media Depth Filter/Carbon Column Effluent	Standards BPCTCA	Standards BATEA
COD (mg/ℓ)	71	500	130
BOD_5 (mg/ℓ)	2	10	5
TOC (mg/ℓ)	8	--	--
Suspended Solids (mg/ℓ)	$\sim$10	40	10
Oil and Grease (mg/ℓ)	< 4	10	5

3. Based on the Effluent Limitations Guidelines Development Document the installed investment for dual-media depth filtration and carbon adsorption is \$1.4 MM for a typical plant (337 metric tons rubber/day). Incorporation of dual-media depth filtration and carbon adsorption can be expected to increase the operating and maintenance costs over BPCTCA by \$0.12/m^3 (\$0.46/1000 gal) to a total treatment cost of \$0.30/m^3 (\$1.12/1000 gal). These cost figures were not verified during this program. Further testing is essential to develop an accurate economic profile of these processes

SOLUTION CRUMB RUBBER

END-OF-PIPE EFFLUENTS

1. Treatment of the end-of-pipe solution crumb effluent by the sequence of ultrafiltration (UF) and reverse osmosis (RO) will produce a high quality effluent, potentially reusable throughout the solution crumb plant. This alternative should be considered for new sources, eliminating the need for primary and secondary treatment and additional processes to meet BATEA standards.
2. Representative data from feasibility tests are compared with BPCTCA and BATEA standards below:

Contaminant	Ultrafiltration/ Reverse Osmosis Effluent	Standards BPCTCA	Standards BATEA
COD (mg/ℓ)	36	245	130
BOD_5 (mg/ℓ)	4	25	5
TOC (mg/ℓ)	10	--	--
Suspended Solids (mg/ℓ)	nil	40	10
Total Dissolved Solids (mg/ℓ)	141	--	--
Oil and Grease (mg/ℓ)	< 5	10	5

3. The net investment required for UF/RO for a typical plant (80.2 metric tons/day) ranges from \$0.87 MM to \$1.2 MM, depending on the selection of UF module geometry. The operating and maintenance costs

(exclusive of concentrate disposal costs and water reuse credits) range from \$0.62/m^3 (\$2.35/1000 gal) to \$0.84/m^3 (\$3.18/1000 gal) depending on the ultrafiltration module geometry.

SECONDARY EFFLUENT

1. Dual-media depth filtration and carbon adsorption treatment of the secondary treated solution crumb wastewater will produce an effluent satisfying BATEA standards, and also potentially reusable. This technology should be considered for all existing sources with primary and secondary treatment currently in place.

2. Representative data from feasibility tests are compared with BPCTCA and BATEA standards below:

Contaminant	Dual-Media Depth Filter/Carbon Column Effluent	Standards	
		BPCTCA	BATEA
COD (mg/ℓ)	72	245	130
BOD$_5$ (mg/ℓ)	4	25	5
Suspended Solids (mg/ℓ)	< 5	40	10
Total Dissolved Solids (mg/ℓ)	820	--	--
Oil and Grease (mg/ℓ)	< 5	10	5

3. Based on the Effluent Limitations Guidelines Development Document and data generated during this program the installed investment for dual-media depth filtration and carbon adsorption is \$0.53 MM for a typical plant (80.2 metric tons/day). Incorporation of dual-media depth filtration and carbon adsorption can be expected to increase the operating and maintenance costs over BPCTCA by \$0.70/m^3 (\$2.66/1000 gal) to a total treatment cost of \$0.91/m^3 (\$3.46/1000 gal).

LATEX RUBBER

END-OF-PIPE EFFLUENT

1. Treatment of end-of-pipe latex rubber effluent is complicated by latex instability. Both ultrafiltration and dual-media depth filtration pretreatment options appear uneconomical. Until some method for suspended solids removal is found, subsequent treatment by carbon adsorption or reverse osmosis to meet BATEA standards cannot be demonstrated.

SECONDARY EFFLUENT

Treatment of secondary effluent from latex rubber manufacture was not studied in this program.

IN-PROCESS EFFLUENT TREATMENT

1. Ultrafiltration (UF) can be employed to treat within-process latex washdown waters. These effluents amount to 70 to 90% of a latex manufacturing plant's total effluent. The recovered latex is potentially suitable for reuse, and the associated credit for by-product recovery helps to defray operating costs.
2. The preferred mode of operation will have recycle of latex washdown waters until their suspended solid concentration reaches 0.5%. This 0.5% solids waste is then to be concentrated by UF to about 15% solids.
3. Representative data from feasibility tests are compared with BTCTCA and BATEA standards below:

Contaminant	Ultrafiltration Effluent	Standards BPCTCA	Standards BATEA
COD (mg/ℓ)	775	500	130
BOD_5 (mg/ℓ)	230	25	5
Suspended Solids (mg/ℓ)	< 5	40	10
Oil and Grease (mg/ℓ)	--	10	5

4. BPCTCA and BATEA standards for the total plant should be achievable by primary and secondary treatment of the remaining 10%-30% of the process wastewater and secondary treatment of the ultrafiltration effluent.
5. Based on data generated during this program the installed investment for ultrafiltration is \$0.16 MM for a typical plant (28.7 metric tons/day). Primary and secondary treatment of the remaining 10%-30% of the process wastewater and secondary treatment of the ultrafiltration effluent would bring the treatment system's total installed cost to \$0.57 MM. The economics of ultrafiltration of latex washdown waters are highly favorable since the annual credits from recovered latex are greater than twice the annual ultrafiltration system operating costs. Because of these credits, the operating and maintenance costs for total latex rubber effluent treatment to meet BATEA standards are projected to be \$0.11/m^3 (\$0.42/1000 gal).

6. Treatment by reverse osmosis of the ultrafiltration effluent has been shown to produce a high quality product water potentially suitable for reuse. An economic analysis of reverse osmosis treatment was not performed during this program.

SECTION 3

RECOMMENDATIONS

It is recommended that pilot-scale field demonstrations be undertaken to verify the performance and projected costs for the preferred treatment technologies. Four demonstrations should be performed:

Synthetic Rubber Subcategory	Preferred Technology
1) Emulsion Crumb	Dual-media depth filtration/activated carbon adsorption for treatment of secondary effluent
2) Solution Crumb (existing facilities)	Dual-media depth filtration/activated carbon adsorption for treatment of secondary effluent
3) Solution Crumb (new sources)	Ultrafiltration/reverse osmosis for treatment of end-of-pipe effluent
4) Latex	Ultrafiltration of within process latex washdown waters; primary/secondary treatment of remaining wastes and secondary treatment of the ultrafiltration effluent

SECTION 4

PROJECT OBJECTIVES AND SCOPE

PROJECT OBJECTIVES

The overall objective of this program was to evaluate alternative advanced wastewater treatment technologies for synthetic rubber wastes and to determine which unit processes or combinations of processes are the most cost-effective for reducing the pollutant loadings to BATEA standards. The BATEA guidelines were proposed based on tertiary treatment with activated carbon or alternative technologies for treating synthetic rubber manufacturing wastewaters. An assessment of the feasibility and economics of carbon adsorption and alternative technologies for direct application to raw wastes and supplemental application to secondary effluents was therefore warranted.

PROJECT SCOPE

This evaluation was performed at a pilot scale in the laboratories of the Walden Division of Abcor, Inc. Process feasibility tests were conducted with actual wastewater samples collected in the field.

The principal unit processes investigated were:

- carbon adsorption,
- reverse osmosis, and
- ozonation.

For each of these processes, waste pretreatment for suspended solids removal is required. Suspended solids removal is necessary for maintenance-free operation of the principal unit processes.

The two methods of suspended solids removal investigated were:

- ultrafiltration, and
- depth filtration (dual-media).

Product waters from the reverse osmosis and carbon adsorption processes received ozonation posttreatment.

Sufficient information is currently available to assess the pollutant removal efficiencies and costs for conventional primary and secondary treatment. This program, therefore, concentrated on the evaluation of alternative technologies which can either supplement or replace the conventional ones. It provided an overview of the applicability of available treatment methods through the use of feasibility experiments. Definitive studies of the wastewater treatment problems associated with this industry will, however, require future field demonstration programs.

The program consisted of three main tasks:

1. An Evaluation of the Proposed BATEA Treatment Method.
2. An Evaluation of Alternative Advanced Wastewater Treatment Processes.
3. Selection of Preferred Process Options Based Upon Technical Performance and Estimated Costs.

Tasks 1 and 2 were conducted simultaneously with the candidate unit processes evaluated with actual waste streams from emulsion crumb, solution crumb, and latex rubber manufacturing. Three types of wastewaters were evaluated: end-of-pipe, secondary treated, and in-process. End-of-pipe, or raw, wastewaters refer to combined plant waste streams before primary or secondary treatment. Secondary treated wastewaters refer to the effluent from conventional biological treatment. In-process wastes refer to streams which have the potential to be reused if effective dewatering can be achieved. The in-process wastes were collected prior to their integration with (and contamination by) the remaining plant wastewater streams.

The six waste streams studies are identified in Table 7. A characterization of each waste stream is presented in a subsequent section.

TABLE 7. DESCRIPTION OF SYNTHETIC RUBBER MANUFACTURING WASTE STREAMS SAMPLED

No.	Manufacturing Process	Sampling Location	Synthetic Rubber Type(s)
1	emulsion crumb	end-of-pipe	SBR
2	emulsion crumb	secondary treated	SBR
3	solution crumb	end-of-pipe	polybutadiene & polyisoprene
4	solution crumb	secondary treated	polybutadiene & polyisoprene
5	latex	end-of-pipe	SBR
6	latex	in-process	SBR and polybutadiene

Based on the results of Tasks 1 and 2, preferred process options were selected, and full-scale system economic projections were developed for each type of rubber manufacturing plant. Again, field demonstrations of the preferred processes will be required before detailed engineering and economic evaluations can be made.

SELECTION OF UNIT PROCESSES FOR EVALUATION

A block diagram showing the alternative combination of the unit operations investigated is presented in Figure 5. Various combinations were employed for each waste type and only potentially promising combinations were investigated in each case.

Dual-media depth filtration and ultrafiltration were the two pretreatment alternatives chosen for evaluation. Dual-media (anthracite/silica sand) filtration has been recommended by the EPA to remove suspended solids from secondary-treated effluents prior to further BATEA treatment. Dual-media depth filtration of secondary-treated (biological and chemical) municipal wastewaters with average influent suspended solids loadings of 12-13 mg/liter has shown suspended solids removals ranging from 33% to 90% (6). Depth filtration with single, dual, and multi-medias is employed extensively in full-scale municipal and industrial waste treatment installations both as an intermediate process (prior to carbon adsorption, ion exchange or reverse osmosis) and as a final polishing step. The advantages of depth filtration include:

- low capital cost,
- low operating cost, and
- simple operation.

On the other hand, depth filters cannot process waste streams with high suspended solids loadings without encountering severe surface blinding. The surface blinding rapidly increases the headloss through the filter resulting in short filtration cycles.

Ultrafiltration is a membrane separation process which can achieve essentially complete rejection of suspended solids at very high water recoveries. Therefore, for synthetic rubber manufacturing wastes where high suspended solids loadings are encountered (i.e., raw emulsion crumb and raw latex wastewaters) ultrafiltration pretreatment has been selected. In a number of cases, ultrafiltration systems can be used for the simultaneous reduction in overall pollutant loading from a manufacturing site and for the concentration and recovery of valuable products or by-products. The potential exists for the recovery and reuse of latex from certain latex wastewater streams.

Carbon adsorption, reverse osmosis, and ozonation were the principal treatment unit operations investigated. Carbon adsorption is currently the

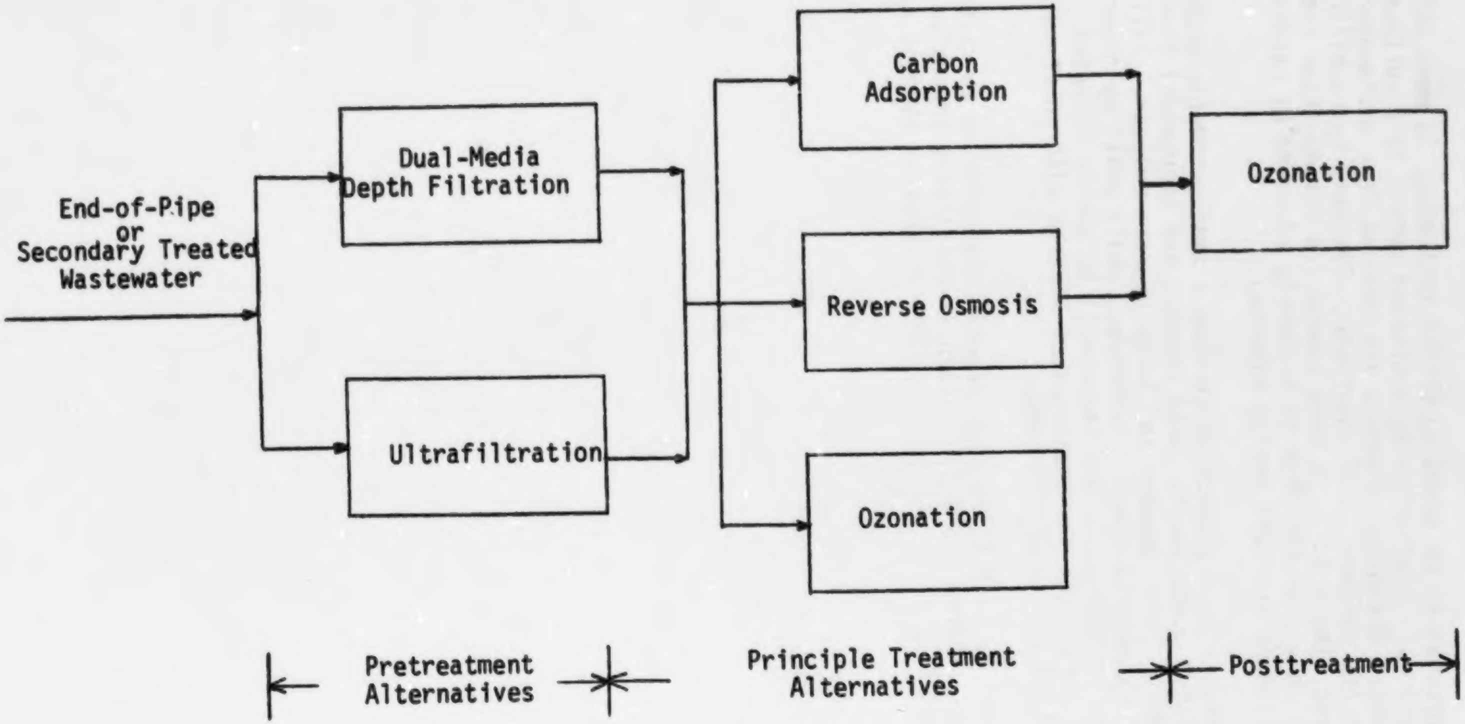


Figure 5. Block diagram of alternative combinations of unit process investigated.

proposed unit process to be added to BPCTCA technology to meet BATEA effluent limitations. Adsorption by activated carbon is a surface phenomenon in which dissolved organics are removed from wastewater and concentrated at the carbon-liquid interface. The more hydrophilic the organic, the less likely it is to move toward the carbon-water interface. Thus, highly soluble organics tend to be poorly adsorbed by carbon; whereas less soluble organics are more highly adsorbed.

Reverse osmosis is a process which uses a semi-permeable membrane to remove dissolved contaminants (both organic and inorganic) from wastewater. In general, ionic species and large organic molecules will be highly rejected by reverse osmosis membranes, while small hydrogen-bonding organics and non-ionized acids and bases will be poorly rejected. Reverse osmosis is best suited for the treatment of streams with intermediate solute concentrations (500 ppm to 20,000 ppm).

Ozonation can be used to oxidize organic contaminants to carbon dioxide and water. Since ozone generation is relatively expensive, it is used most economically after activated carbon or reverse osmosis as a polishing step.

SECTION 5

EXPERIMENTAL PROCEDURES

WASTE COLLECTION AND CHARACTERIZATION

Introduction

Approximately 2 m^3 (500 gal) samples of each wastewater type, except for latex washdown waters, were obtained from synthetic rubber manufacturers. These samples were preserved by pH adjustment to suppress biological activity and shipped via truck to the pilot test facilities. The BOD_5 of the wastes were measured on-site prior to shipment and again upon their arrival at the pilot plant to monitor any change in their chemical composition. The samples were neutralized prior to testing and were processed as soon after receipt as was logistically possible.

For the in-process latex wastewater samples, several different types of latex and latex washdown water were obtained. Sample volumes ranged from 1.89×10^{-2} m^3 (5 gal) to 0.76 m^3 (200 gal) depending on the specific tests to be conducted. The pH of these samples was not adjusted since this could have resulted in destabilization and coagulation of the latex solids (0.5 wt % to 20 wt %).

A brief characterization of each wastewater tested is presented below.

Emulsion Crumb Waste Samples

End-of-Pipe Emulsion Crumb Wastewater--

The raw emulsion crumb (REC) wastewater sample obtained was the combined effluent from five different SBR production lines. These rubbers were produced simultaneously and are described by industry code (to the nearest approximation) in Table 8. No mixing with NBR wastes occurred at the point of sampling.

TABLE 8. DESCRIPTION OF SBR TYPES BEING PRODUCED BY THE EMULSION CRUMB PROCESS AT THE TIME OF RAW WASTE SAMPLING

Industry Code	Description
1. 1502	SBR non-oil extended, non-stainer
2. 1712	SBR oil extended, stainer type AO oxidant stabilizer
3. 1778	SBR oil extended, non-stainer stabilizer
4. 1808	SBR oil black master batch; oil extended, carbon black, stainer type AO oxidant stabilizer
5. No industry code	SBR oil extended, stainer type AO oxidant stabilizer

The contaminant loadings for the resulting waste stream, as shown in Table 9, were comparable to the REC mean waste loadings for COD, BOD_5 and suspended solids as reported in the Development Document (4). The oil concentration of the raw waste was substantially below the mean value, but was consistent with some individual point source determinations reported. The suspended solids and oil determinations were made downstream of the crumb pits in both instances.

TABLE 9. COMPARISON OF SAMPLED REC WASTE STREAM AND DEVELOPMENT DOCUMENT ANALYTICAL DATA

Assay	Development Document Mean Waste Loading	Sampled Waste Stream
COD (mg/ℓ)	1,177	879
BOD (mg/ℓ)	154	119
Suspended Solids (mg/ℓ)	398	191
Oil and Grease (mg/ℓ)	90	12

The pH of the emulsion crumb raw waste sample was adjusted with concentrated sulfuric acid to approximately 4.0 before shipment in order to maintain sample integrity. As shown in Table 10, little change in the sample BOD_5 or COD was observed during transportation and storage.

TABLE 10. BOD_5 AND COD ANALYSES FOR RAW EMULSION CRUMB WASTEWATER

Sampling Date	BOD_5 (mg/ℓ)	COD (mg/ℓ)
15 October (at SBR plant)	119	879
23 October	90	---
30 October	98	917
4 November	140	---
14 November	96	---
18 November	96	---

Secondary-Treated Emulsion Crumb Wastewater--

The secondary-treated emulsion crumb (SEC) effluent was obtained from the same plant as the REC wastewater. Primary treatment at the plant consists of wastewater flocculation, settling, and sludge removal. For secondary treatment, the primary effluent is passed through four bio-oxidation lagoons. The first three lagoons are aerated in decreasing amounts, while the fourth lagoon is quiescent.

Due to a reduced production schedule, no NBR was produced prior to sampling. Based on the lagoon retention times, it was estimated that the wastewater was 0.5% to 1.0% NBR waste. Also, wastewaters from other plant areas - rain water, antioxidant-plant wastewater, and sanitary sewage - are passed through the primary and secondary treatment processes.

The sample was pH adjusted with sulfuric acid to prevent continued biological activity during shipment. BOD_5, COD, and TOC analyses of the sample taken before shipment and during processing are summarized in Table 11. Little (if any) sample degradation can be inferred from the TOC and COD results.

TABLE 11. BOD_5, COD, AND TOC ANALYSES FOR SECONDARY TREATED EMULSION CRUMB WASTEWATER

Sampling Date	pH	BOD_5 (mg/ℓ)	COD (mg/ℓ)	TOC (mg/ℓ)
31 December (at SBR plant)	<4	7	260	--
14 January	2.3	< 1	372	72
15 January	7.1	40	206	72
19 January	7.1	16	---	70
27 January	5.6	--	---	68

Solution Crumb Waste Samples

End-of-Pipe Solution Wastewater--

The raw solution crumb (RSC) wastewater stream sampled was generated by the production of solution crumb rubbers, adhesives, and antioxidants. Approximately 70% of the wastewater is attributed to solution crumb rubber manufacture. Of this volume, two-thirds comes from the production of polyisoprene rubber.

Table 12 compares the analytical results for the RSC sample to the mean results reported for this waste in the Development Document. The on-site analyses were performed in duplicate and the average values are given.

TABLE 12. COMPARISON OF THE SAMPLED RSC WASTE STREAM AND DEVELOPMENT DOCUMENT ANALYTICAL DATA

Assay	Development Document Mean Waste Loading	On-Site Sample Analysis (average)	Walden Sample Analysis
Suspended Solids (mg/ℓ)	169	29	201
COD (mg/ℓ)	542	569	584
BOD_5 (mg/ℓ)	68	> 48	95
Oil and Grease (mg/ℓ)	65	---	28*

* Assay performed after pH adjustment of total sample shipment to pH=11. Original sample pH=8.

The suspended solids loading, as measured in the field prior to shipment, is substantially below the Development Document mean value (169 mg/ℓ) and the Walden laboratory analysis (201 mg/ℓ) and is possibly in error. The waste oil and grease loading is highly dependent on the type of rubber being produced. Since the majority of production at the time of sampling was geared to "non-extended" rubbers, the relatively low oil and grease content in the sampled wastewater would be expected.

Analytical results for BOD_5, COD, and TOC before shipment and during processing of the sample are given in Table 13. These results indicate no substantial degradation of the waste sample.

TABLE 13. BOD_5, COD, AND TOC ANALYSES FOR END-OF-PIPE SOLUTION CRUMB WASTEWATER

Sampling Date	pH	BOD_5 (mg/ℓ)	COD (mg/ℓ)	TOC (mg/ℓ)
27 February (at PBR/IR plant)	> 10	> 50/45	563/575	---
5 March	11.1	95	584	140
9 March	8.2	86	625	144

Secondary-Treated Solution Crumb Wastewater--

The secondary-treated solution crumb (SSC) effluent was obtained from the same manufacturing plant as the RSC wastewater. The wastewaters from the solution crumb rubber production lines are combined with wastewaters from other plant areas, including storm water, monomer plant, and chemical plant, prior to primary and secondary treatment.

The effluents from the crumb rubber production lines are skimmed to remove free oil prior to combination with the polybutadiene production and utility water streams. The wastewater treatment system consists of an equalization pond, a neutralization basin, two parallel activated sludge/aeration basins and a final clarifier.

No analyses were performed on-site on the sampled wastewater. The sample was pH adjusted with NaOH to prevent biological activity during shipment.

Latex Waste Samples

End-of-Pipe Latex Wastewater--

The raw latex wastewater (RLX) sample was collected during a period of 100% SBR production (i.e.. no NBR production wastes included) and was taken from a 113 m^3 (30,000 gal) holding basin prior to primary treatment. At the time of sampling, 90% of the plant production was involved in manufacturing three different latices. The industry codes for these latices are as follows:

Industry Code	Percentage
5352	40%
- (similar to 5352)	40%
2108	10%
Miscellaneous	10%

Table 14 compares the analytical results for the RLX sample to the mean results reported for this waste in the Development Document.

TABLE 14. COMPARISON OF SAMPLED RLX WASTE STREAM AND DEVELOPMENT DOCUMENT ANALYTICAL DATA

Assay	Development Document Mean Waste Loading	Sampled Waste Stream
COD (mg/ℓ)	2,620	482
BOD_5 (mg/ℓ)	398	> 340
Suspended Solids (mg/ℓ)	463	133
Oil and Grease (mg/ℓ)	25	41

The Development Document mean waste loading was determined after sampling two latex plants, only one of which was 100% SBR (4). Process variations between plants and daily operational changes within each plant preclude both complete wastewater characterization and uniformity.

A gradual decline in the wastewater BOD_5 took place during the testing period (see Table 15). Inconsistencies in the wastewater COD analyses noted in this Table are not readily explainable.

TABLE 15. BOD_5 AND COD ANALYSES FOR RAW LATEX WASTEWATER

Sampling Date	BOD_5 (mg/ℓ)	COD (mg/ℓ)
20 November (at SBR plant)	> 340	482
4 December	240	1350
8 December	100	----
18 December	66	----

In-Process Latex Washdown Waters--

Four latex washdown water (LWW) streams considered typical of the in-process wastewaters requiring treatment at a styrene-butadiene latex manufacturing plant were tested. The streams contained latex concentrations of 0.6%, 3.6%, 11.4%, and 17.5%.

Chemical analyses (other than total solids) were performed only on the 3.6% latex sample. The analytical results were:

Assay	3.6% Latex Washdown Stream
BOD_5 (mg/ℓ)	1,400
COD (mg/ℓ)	99,200
TOC (mg/ℓ)	23,800

The pH of the LWW samples was not adjusted.

EXPERIMENTAL TEST SYSTEMS AND PROCEDURES

Dual-Media Depth Filtration

Two dual-media depth filtration test systems were employed whenever depth filtration was evaluated for waste pretreatment. A 0.23 m (9-inch) diameter column (0.04 m^2) provided an efficient means of treating large volumes of waste for subsequent reverse osmosis, carbon adsorption, and ozonation tests. A smaller, 0.05 m (2-inch), diameter column (0.002 m^2) provided detailed waste loading, headloss, and backflush requirement data. Both dual-media depth filters processed wastewaters on a once-through basis.

Each depth filter test system had similar operating features. The flow schematic, presented in Figure 6, is applicable to both systems; however, some of the information included is specific to the 0.05 m diameter column. The smaller column was constructed of translucent polycarbonate (Lexan®) allowing visual inspection of the media. Surface caking and/or stream channeling could thus be observed and corrected. The 0.23 m diameter column was a commercial unit (Culligan No. 3329-35 equipped with Culligan control assembly No. 3305-26). The feed solution was transferred from the holding tank to the uppermost portion of the column by a metering pump (centrifugal pump for larger system). The feed percolated through 0.5 m of 1.8 mm anthracite coal followed by 0.25 m of 0.55 mm silica sand. The intermix zone within the column was 0.083 m while the backflush expansion height was 0.17 m. The media was supported by a fine-mesh screen and a perforated plate used to evenly distribute the backwash flow. The inlet pressure to the filter bed and the filtrate turbidity were measured. The flow rate through the column was maintained at 117 m^3/m^2-day (2 gpm/ft^2). The feed solution was at ambient temperature.

During regeneration, filtrate was fed through the base of the column, and the media bed was expanded to the full column height. The backwashing was typically performed for 5 to 8 minutes at a flow rate of 880 m^3/m^2-day (15 gpm/ft^2). The backwash liquid was collected in a holding tank and sampled.

The regenerated column was forward rinsed with the next feed solution to be processed just prior to the initiation of a new test. This "sweetening" of the column acclimated the media to the new wastewater. Forward rinsing was performed for approximately 15 minutes at the normal processing flow rate. The rinse effluent was recycled allowing the entire forward rinsing operation to be performed with a minimal solution volume.

Ultrafiltration

A simplified flow schematic of the ultrafiltration test system is shown in Figure 7. The feed solution was pumped into a 5.68 m^3 (1500 gal) feed tank and was pH adjusted with either concentrated sulfuric acid or 2N sodium hydroxide. The tank contents were agitated throughout the experiment by a mechanical stirrer (Lightening NLDG 150, Type CJ43, 1.1 kW).

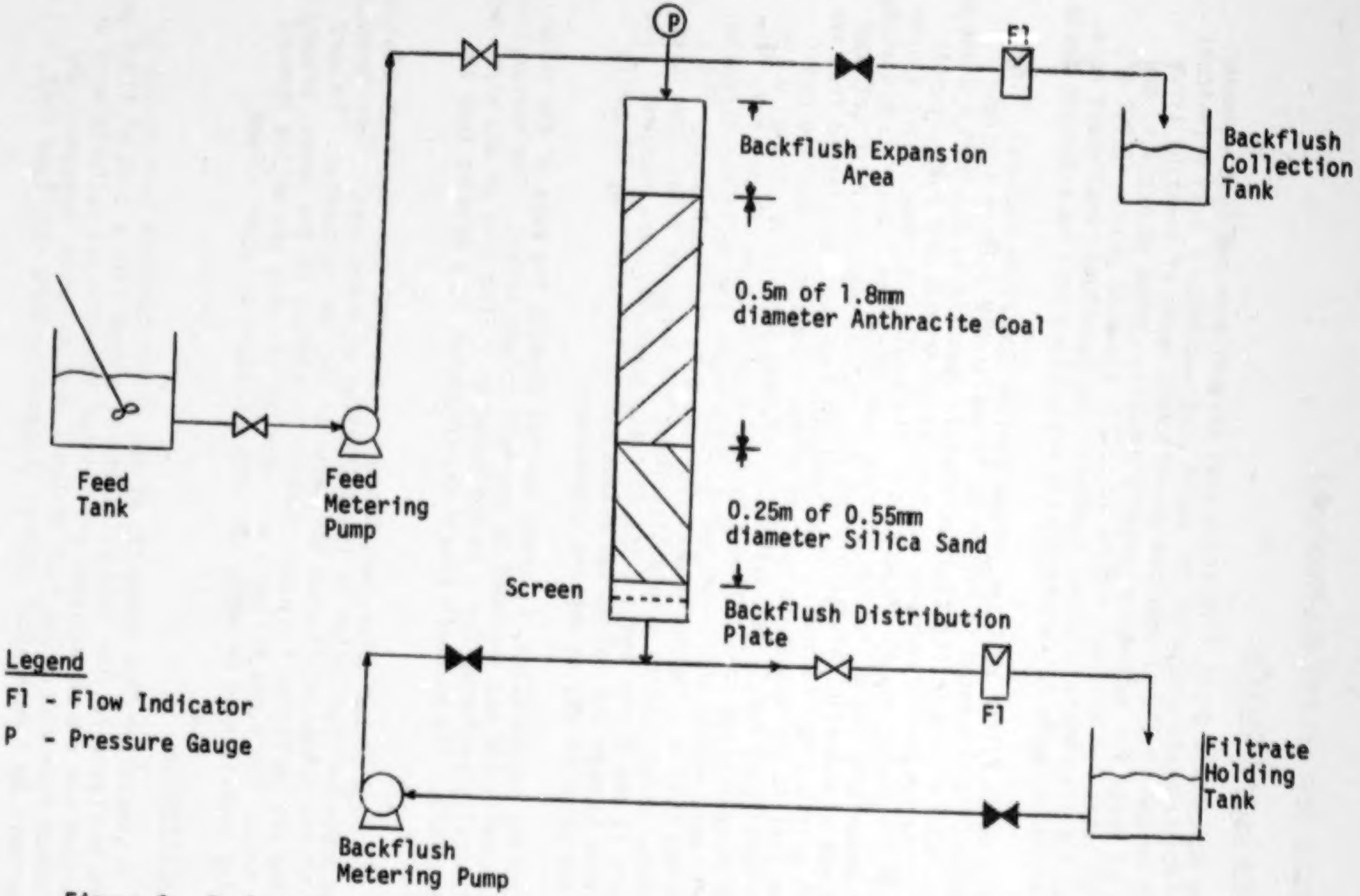
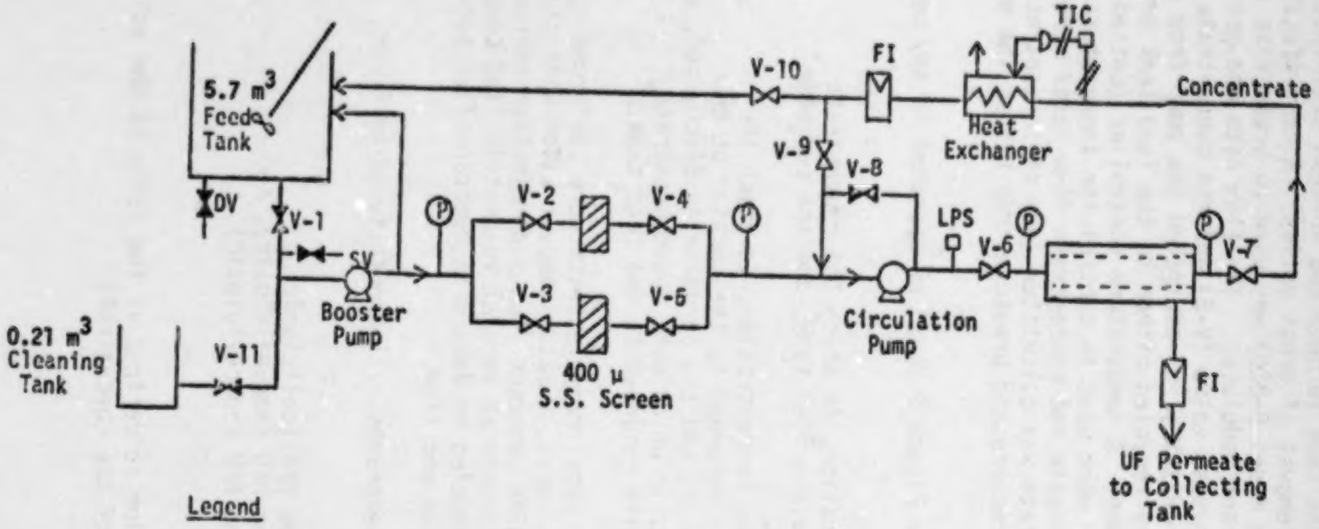


Figure 6. Dual-media depth filtration test system (0.05m diameter column) flow schematic.



Legend

DV - Drain Valve
FI - Flow Indicator
LPS - Low Pressure Switch
P - Pressure Indicator
SV - Sample Valve
TIC - Temperature Indicator/Controller

Figure 7. Simplified flow schematic of ultrafiltration test system.

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A centrifugal booster pump (Dayton Model 6K507) was used to provide sufficient pressure to pass the feed through two 40-mesh stainless-steel strainers, in parallel, for removal of gross solids. A centrifugal circulation pump (Worthington Model D-820) was used to pressurize the feed and pass it through the membrane module(s). The flow rate and pressure were controlled by the pump bypass valve (V-8) and the concentrate throttle valve (V-7). A low pressure switch (LPS) protected the pump from running dry. The concentrate could be recycled either to the feed tank or to the suction of the circulation pump. A temperature controller (United Electric, Type 1200) and heat exchanger were used to control the temperature at a predetermined level. The permeate and concentrate flow rates were measured, and the feed flow rate was calculated (sum of concentrate and permeate flows). The feed pressure and pressure drop across the module(s) were also determined.

The test system shown in Figure 7 could be operated in any one of three different modes:

- batch concentration, in which the concentrate is returned to the feed tank, and the permeate is discharged,
- semi-continuous concentration, in which the concentrate is returned to the suction of the circulation pump, and the permeate is discharged, and
- total recycle, in which both the concentrate and permeate are returned to the feed tank.

In general, preliminary total recycle tests were performed to select the preferred membrane type. Next, a batch concentration with this membrane type was performed to determine membrane flux and rejection characteristics. Finally, total recycle experiments at several volumetric feed concentrations* (e.g., 1X, 5X, 10X) were conducted to determine membrane flux behavior as a function of both concentration and time.

Three ultrafiltration membranes, all manufactured by Abcor, Inc., were tested during this program:

- Abcor Type HFA (cellulosic)
- Abcor Type HFD (noncellulosic), and
- Abcor Type HFM (noncellulosic).

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*Volumetric feed concentration is defined as the ratio of the volume of the initial feed to the volume of the concentrate.

The operating specifications for these three membranes are:

Parameter	HFA	HFD	HFM
Allowable pH Range (at 38°C)	3-8.5	3-12	0.5-12
Maximum Pressure (bar)	3.8	5.2	5.2
Maximum Temperature (at pH 7, °C)	49	85	94
Free Chlorine Tolerance Level	nil	nil	50 ppm

Two different module configurations were evaluated during the ultrafiltration tests: tubular and spiral-wound. The tubular membrane elements, as shown in Figure 8, consisted of a porous fiberglass support tube 0.025 m (1-inch) in diameter by 3.0 m (10-ft) long with the membrane cast on the inside surface of the tube. Each tube contained a membrane surface area of 0.20 m^2 (2.2 ft^2). The "module" consisted of eight of these tubes connected in series. All three membrane types were evaluated in the tubular configuration.

An Abcor Type HFM corrugated-spacer, spiral-wound module was evaluated during tests with the end-of-pipe emulsion crumb wastewater. The module configuration is depicted in Figure 9. The spiral module, 0.10 m (4-inch) in diameter x 1.22 m (4-ft) long, had a membrane surface area of 3.2 ± 0.2 m^2 (34 ± 2 ft^2) and was tested in parallel with a tubular module.

The membrane modules were cleaned with "Ultra-Clean", a commercially available membrane cleaning solution (Abcor, Inc.), before each experiment to remove foulants from the membrane surface.

The typical values of the operating parameters for the ultrafiltration tests were:

System Feed Pressure	3.45 bar
Feed Temperature	38°C
Circulation Flow Rate	
Tubular Modules	6.8 m^3/hr
Spiral-wound Modules	22.7 m^3/hr
Volumetric Concentration Ratio Achieved	10X - 20X

The degree of volumetric concentration achieved was generally limited by the holdup volume of the test system and the sample volume and was not a process limitation.

Reverse Osmosis

A simplified flow schematic for the reverse osmosis test system is presented in Figure 10. The pretreated synthetic rubber wastes (dual-media depth filter effluent or ultrafiltrate) were transferred to the 5.68 m^3 (1500 gal) RO feed tank. A booster pump (Dayton Model 6F507) was used to

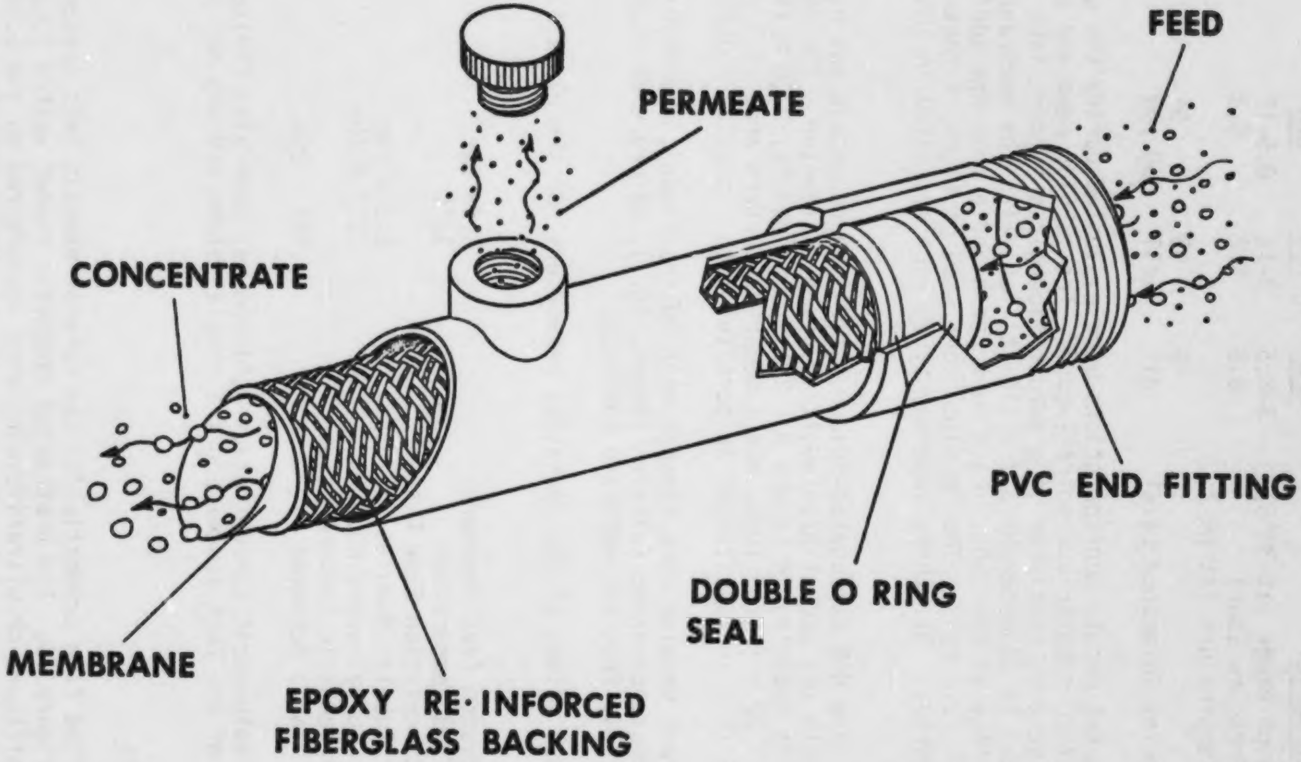


Figure 8. Cutaway view of tubular ultrafiltration membrane element.

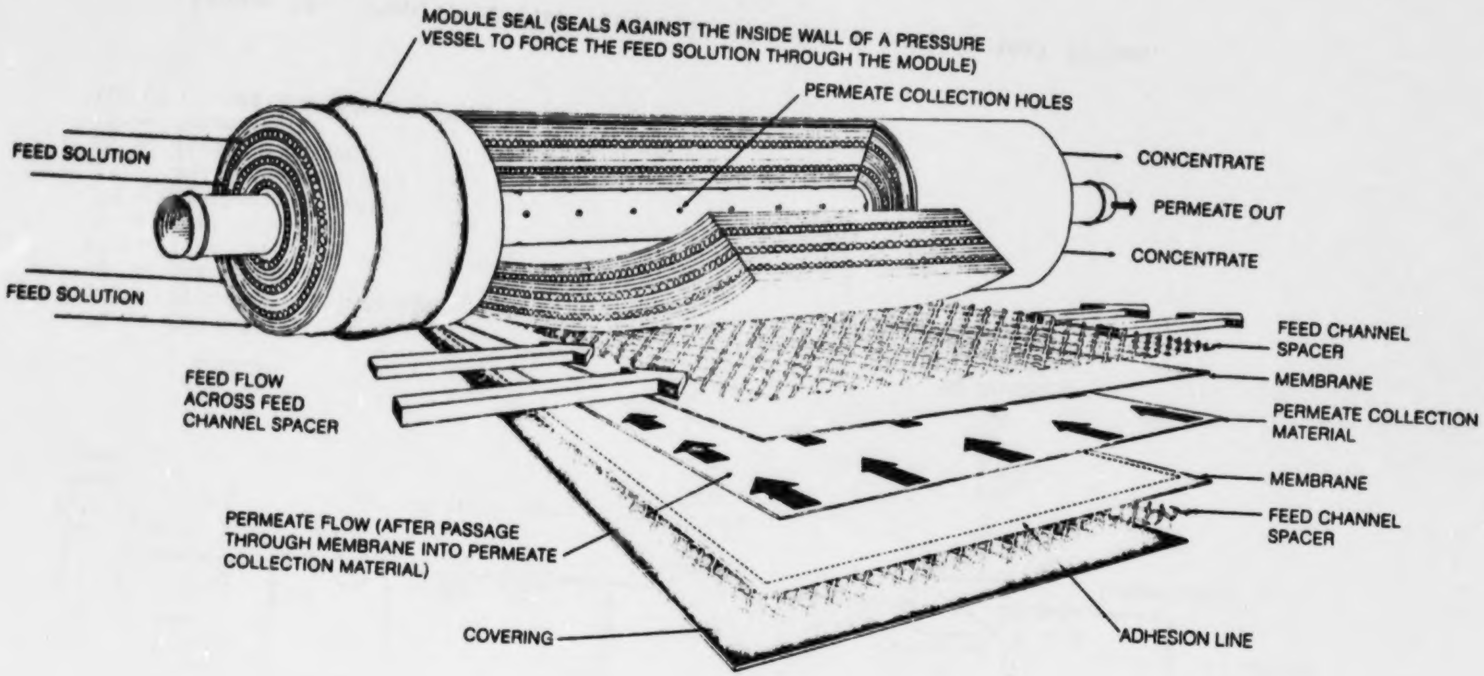
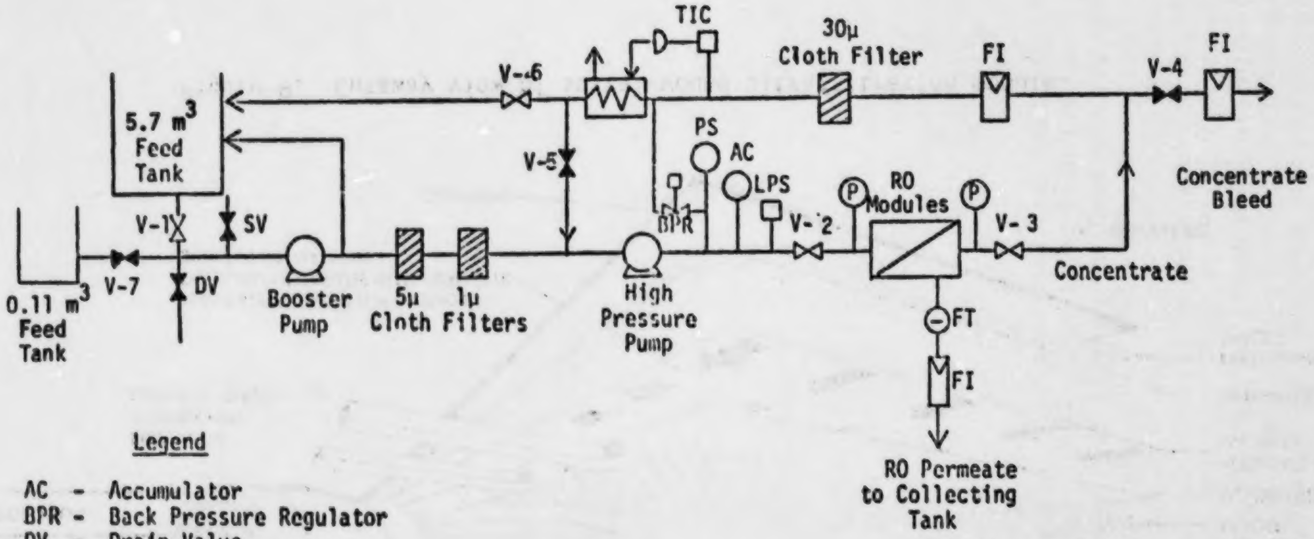

MODULE SEAL (SEALS AGAINST THE INSIDE WALL OF A PRESSURE VESSEL TO FORCE THE FEED SOLUTION THROUGH THE MODULE)
PERMEATE COLLECTION HOLES
FEED SOLUTION
CONCENTRATE
PERMEATE OUT
CONCENTRATE
FEED SOLUTION
FEED CHANNEL SPACER
MEMBRANE
FEED FLOW ACROSS FEED CHANNEL SPACER
PERMEATE COLLECTION MATERIAL
MEMBRANE
PERMEATE FLOW (AFTER PASSAGE THROUGH MEMBRANE INTO PERMEATE COLLECTION MATERIAL)
FEED CHANNEL SPACER
COVERING
ADHESION LINE

Figure 9. Cutaway view of spiral-wound ultrafiltration module.



Legend

AC - Accumulator
BPR - Back Pressure Regulator
DV - Drain Valve
FI - Flow Indicator
FT - Flow Totalizer
LPS - Low Pressure Switch
P - Pressure Indicator
PS - Pressure Switch
SV - Sample Valve
TIC - Temperature Indicator/Controller

Figure 10. Simplified flow schematic of reverse osmosis test system.

pass the feed through two string-wound cartridge filters, in series, to the suction of the high-pressure positive-displacement pump. This pump (Gaulin Model 75E) increased the feed pressure to 28-55 bar (400-800 psig). The feed pressure was controlled by the back pressure regulator (BPR), and the flow rate through the module was controlled by the concentrate throttle valve (V-3). An accumulator (AC) was used to dampen pressure pulsations from the pump. The reverse osmosis modules were protected against over-pressurization by a high pressure switch (PS), and the pump was protected against running dry by a low pressure switch (LPS). The feed temperature was measured and controlled by an indicating temperature controller (United Electric, Type 1200). The flow rates of the permeate and concentrate were measured, and the feed flow rate was calculated (sum of permeate and concentrate flow rates). The feed pressure and pressure drop across the module were also measured.

The reverse osmosis test system was similar to the ultrafiltration test system in that it could be operated in one of three modes: batch concentration, semi-continuous concentration, and total recycle. Also, a series of tests similar to the ultrafiltration experiments for module selection and module performance characterization were performed.

Three different commercially available membrane modules were tested:

- a B-9 polyamide membrane in a hollow-fine-fiber configuration (duPont, Inc. Permasep Products Division),
- a B-10 polyamide membrane in a hollow-fine-fiber configuration (duPont, Inc. Permasep Products Division), and
- a ROGA HR 4160 cellulose acetate (CA) membrane in a spiral-wound configuration (UOP, Inc. Fluid Systems Division).

The operating specifications for these membranes are:

Parameters	B-9	B-10	HR 4160
Allowable pH range	4-11	5-9	4-6
Maximum Pressure (bar)	28	55	41
Maximum Temperature (°C)	35	30	30

The construction and operation of a hollow-fiber module is shown in Figure 11. Pressurized feed is passed over the hollow-fiber membranes, and water permeates to the interior of the hollow fibers and is collected as permeate. The membrane surface area for hollow-fine-fiber modules is very high, and flux values based on a unit area of membrane surface are often misleading. Therefore, the "productivity" (permeate flow per module) is reported rather than flux per se. The construction of a spiral-wound reverse osmosis module is similar to that shown for a spiral-wound ultrafiltration module (see Figure 9).

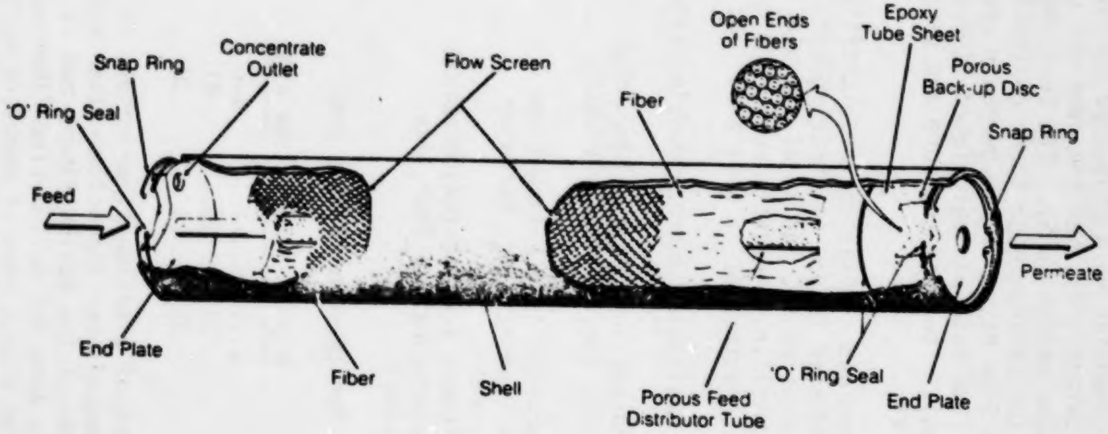


Figure 11. Cut away drawing of Permasep permeator.

At certain points during the reverse osmosis tests, it became necessary to clean the modules with a citric acid solution. Following cleaning, the B-10 module required treatment with PT-B, a membrane "tightening agent".

Typical values of the operating parameters for the reverse osmosis tests with synthetic rubber manufacturing wastes were:

System Feed Pressure	28-55 bar (dependent on module)
Feed Temperature	27-30°C
Feed Flow Rate	1.1 m^3/hr
Volumetric Concentration Ratio Achieved	Up to 20X

Following each reverse osmosis experiment, a standard test was performed to determine if any decline in membrane flux or rejection had occurred. After the system was drained and flushed with dechlorinated water, it was operated in the total recycle mode on a standard NaCl solution (~5000 ppm). The system was operated at the normal module operating pressures, a feed temperature of 26-28°C and a feed flow rate of 1.1 m^3/hr (5 gpm). At steady state, the feed and permeate flows and concentrations were measured, and the measured rejection* was corrected to a module conversion+ of 0%.

Carbon Adsorption

Filtrasorb 400 (Calgon, Inc.), a general-purpose carbon for wastewater treatment, was used for both isotherm and column tests.

Adsorption Isotherms--

The carbon adsorption isotherm tests were conducted using the following procedure:

1. Filtrasorb 400 granular activated carbon was ground with a mortar and pestle and screened to < 45 micron (335 mesh) size.
2. Seven samples of dried carbon were weighed out: 2 mg, 5 mg, 10 mg, 20 mg, 50 mg, 100 mg, and 500 mg.
3. Each sample of dried carbon was placed in a separate erlynmeyer flask.
4. 100 (±1) ml of pretreated wastewater (ultrafiltrate or dual-media depth filter effluent) were added to each flask.

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*Rejection, $r = \frac{\text{Feed Concentration - Permeate Concentration}}{\text{Feed Concentrate}} \times 100\%$

+Conversion, $y = [1 - (1/\text{Volumetric Feed Concentration})] \times 100\%$

5. The flasks were stoppered and placed on a Burrel Wrist Action Shaker for 24-48 hours.
6. The flask contents were filtered through a 0.22 micron Millipore Filter, and the center portion of filtrate was collected for analysis.
7. The seven carbon treated samples, an original feed sample taken through all procedures except for carbon addition, an original feed sample not taken through the isotherm procedures, and a high purity water sample were analyzed for TOC on a Dohrmann DC-50 TOC analyzer.
8. The data were fit to a Freundlich Isotherm Expression (7) by plotting, on log-log paper. X/m, the amount of pollutant adsorbed per unit weight of carbon versus C, the residual pollutant concentration, and drawing the best straight line through the points.

Column Studies--

The carbon column test system consisted of four columns in series and is shown schematically in Figure 12. Each column was 0.006 m (0.25-inch) diameter x 0.91 m (3-ft) long and constructed of clear polycarbonate (Lexan ®). The feed solution (ultrafiltrate or dual-media depth filter effluent) could be delivered to either the top (downflow mode) or bottom (upflow mode) of the first column by a metering pump (March Mfg. Co., Model 210-5R). This pump was equipped with an accumulator to dampen pressure pulsations. The feed flow rate was maintained at 455 m^3/m^2-day (7.75 gpm/ft^2). Sample valves and air bleed valves were located on each column. The effluent from the last column was collected in a holding tank after discarding the first 0.15 liter (0.04 gal) that passed through the columns (liquid hold-up in system). Samples from each column were taken for TOC analysis after approximately 0.02, 0.05, 0.07, 0.09, and 0.11 m^3 (6, 12, 18, 24, and 30 gal) had been collected in the effluent holding tank. The inlet pressure to the first column was monitored.

The small carbon column ID, 0.006 m, was necessitated by the 0.11 m^3 (30 gal) sample volume available for testing. Comparison tests between this column and a 0.025 m (1-inch) ID column using a known feed solution (1000 ppm isopropyl alcohol) produced similar breakthrough curves as shown in Figure 13.

Ozonation

The flow schematic for the ozonation test system is shown in Figure 14. Purified oxygen ($<$ 40°C dew point) was delivered at 2.8 bar (40 psig) to the ozone generator (W.R. Grace, Model LG-2-L2) which had an internal regulator (PR) to control the feed pressure between 0 and 1 bar (0 and 15 psig) and an internal flow meter to measure the output, 0.283-2.83 m^3/hr @ STP (10-100 SCFH). Ozone was generated in a corona discharge and delivered to

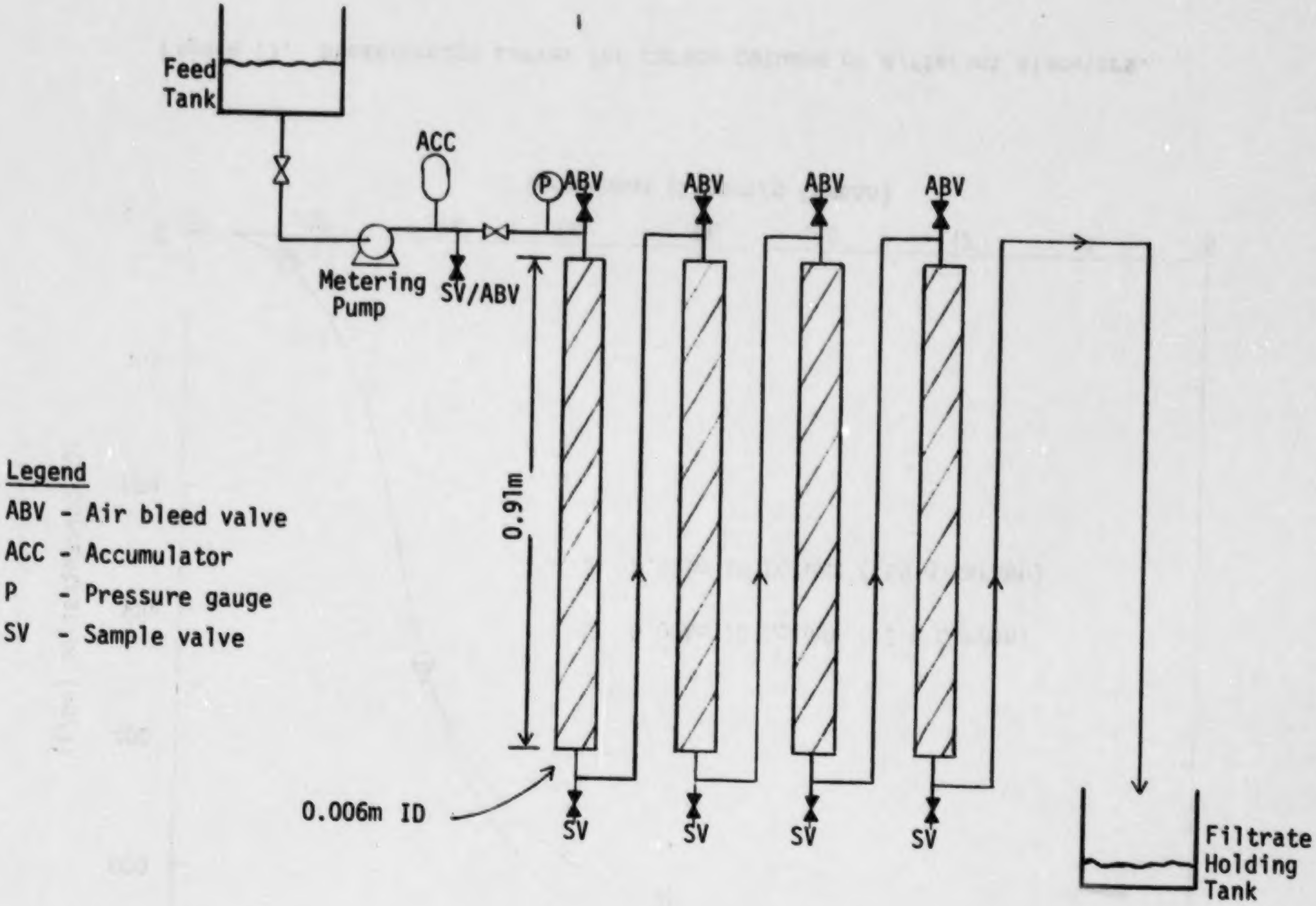

Figure 12. Carbon adsorption test system flow schematic (downflow processing mode).

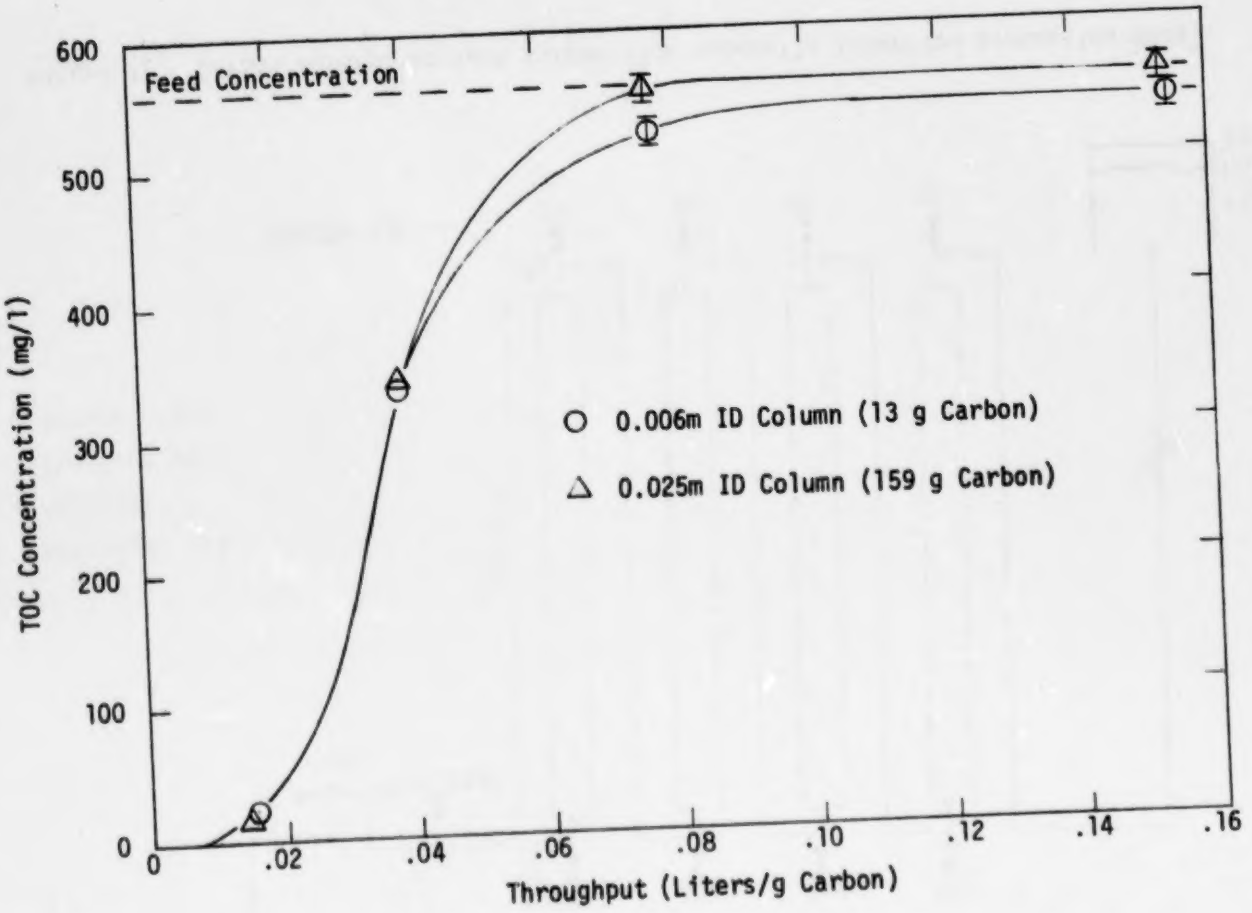

Figure 13. Breakthrough curves for carbon columns of different diameters.

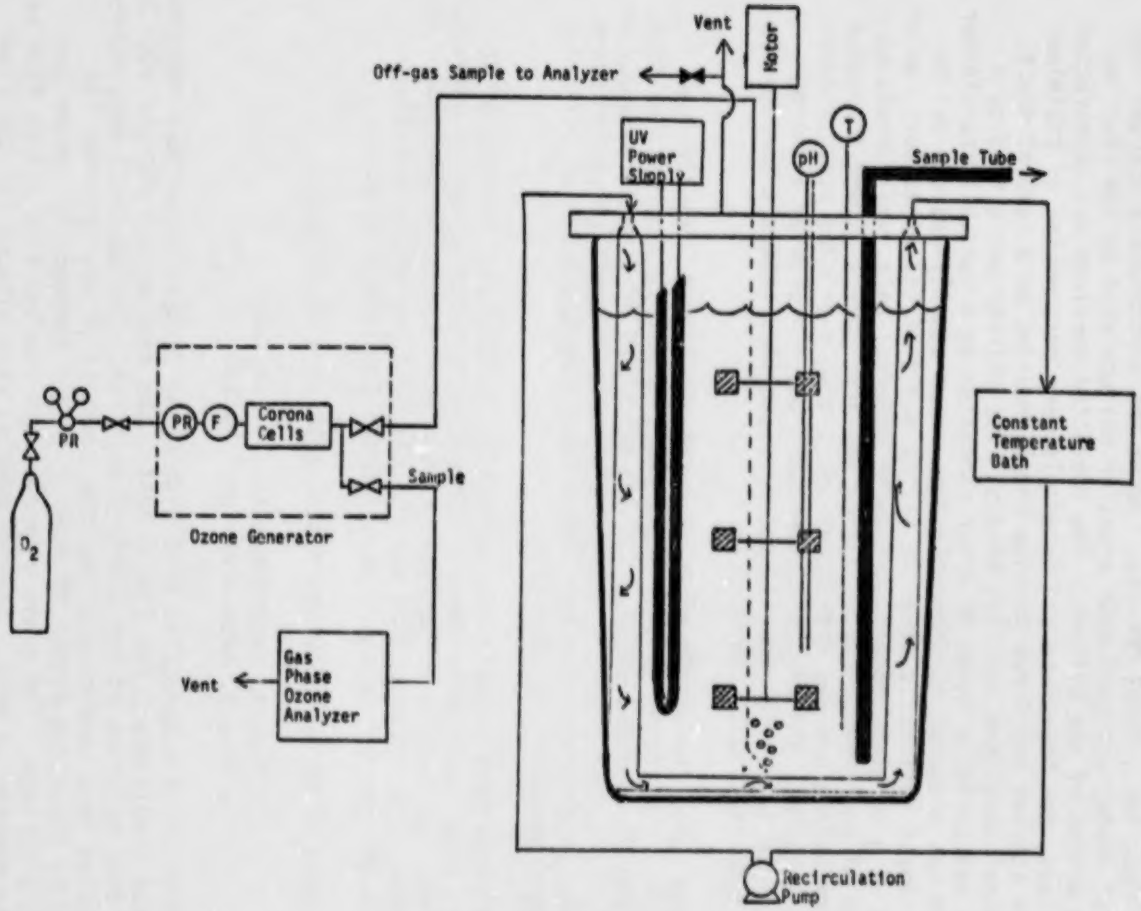

Figure 14. Ozonation test system.

the contacting system through a flow control valve. A sample valve was used to periodically divert a portion of the flow for analysis.

The waste was ozonated in a semi-batch mode (liquid batch with continuous ozone input) using a 14 liter fermenter (New Brunswick Scientific Co., Inc., Model MMF-14). Ozone was continuously sparged into the batch of waste, and good mass transfer was achieved by the shearing and mixing action of the stirrer. The contactor envelope was constructed of Pyrex glass; the top-plate and internals were constructed of stainless steel. The stirrer had three turbine wheels mounted on a central shaft, and each wheel contained six flat blades. The stirrer was driven by a 373 W (0.5 hp) variable speed AC motor connected to a variable transformer. Stirrer RPM was measured stroboscopically. Four equally-spaced, hollow baffles extended vertically down the inside walls of the contactor. Water, maintained at a constant temperature by an external bath, was circulated through two of the interconnected hollow baffles. Ozone flowed through a third hollow baffle and was introduced via a single-orifice sparger below the bottom turbine. The reactor temperature was measured by a thermocouple inserted into a thermowell, and pH electrodes extended through the top-plate into the liquid phase.

In some runs, the effect of UV light on the rate of reaction was investigated. For these runs, UV light was produced by a germicidal lamp (Hanovia Lamp Div., Model 688A45) with an output of 10.2 watts at 253.7 nm (half-width of output peak < 1 nm). The absorption coefficient for ozone is a maximum at this wave length. The U-tube lamp was immersed directly in the liquid phase of the reactor.

A stainless steel sample tube extending to the lower portion of the reactor was used to withdraw samples for analysis. During normal operation, this tube was continually purged with a low flow of purified nitrogen. To take a sample, the nitrogen flow was cut off, and the slight positive pressure in the reactor forced liquid through the sample tube.

Two types of batch ozonation experiments were conducted:

- Type A, reaction-rate-limited, and
- Type B, mass-transfer-limited.

The Type A tests were conducted with high ozone dosages to achieve reaction-rate-limited conditions. For Type A tests, the reactor was charged with 10 liters of feed solution at the start of each run. The contents were warmed to the desired test temperature, and the solution pH was adjusted (if necessary) by injecting either 1N NaOH or 1N HCl through the system top-plate with a syringe. The ozone generator was started with all O_3 flow bypassing the reactor to vent. Several minutes were allowed for the flows and concentrations to stabilize.

A time "zero" TOC sample was taken, and the stirrer was brought up to

~800 rpm. Ozone was then sparged into the reactor, and a timer was started simultaneously. The solution pH was manually adjusted during the run as required to maintain the desired pH level. Samples of the reactor contents were taken for TOC and dissolved ozone analyses at 15, 30, 60, 90, and 120 minutes into the run. The gas phase ozone concentrations before and after the reactor were also measured at these times.

The dissolved ozone concentration was determined spectrophotometrically (8). A known volume of the waste was rapidly mixed with an excess of KI solution to quench the decomposition of O_3 and its reaction with organics. The I_2, formed by oxidation of I^-, complexed with excess I^- to form the tri-iodide ion (I_3^-) which was measured spectrophotometrically.

The concentration of ozone in the gas phase, both before and after the reactor, was determined by diverting a small portion of the ozone flow to a chemiluminescent NO_x analyzer (Thermo Electron Corporation) which had been converted to monitor ozone.

Type B (mass-transfer-limited) tests were conducted at high ozone coversion (low ozone dosages) in order to simulate the operation of a practical contactor and determine the amount of ozone consumed for a given reduction in TOC. For these tests, most of the output of the ozone generator was vented directly, and only a small side-stream was passed through an auxiliary flow meter and through the ozone contactor.

During Type B tests, the contactor was charged with 5 liters of waste. The power and flow to the ozone generator were adjusted to give 1 wt % ozone in the generator output stream. The flow rate of the ozone-containing oxygen stream to the contactor was adjusted to give, if possible, a 95% conversion of ozone across the contactor. The lower gas flow rates for the Type B runs (0.028 m^3/hr vs. 1.42 m^3/hr @ STP for Type A) require longer reaction times to achieve appreciable TOC reduction. Thus, Type B runs were continued for six hours with samples taken every hour for TOC analysis. The ozone concentration in the off-gas from the contactor was measured frequently to determine the consumption of ozone.

SAMPLE ANALYSIS

Table 16 lists the assays performed on composite feed, filtrate and concentrate samples from each unit process and the analytical methods employed. Also, grab samples for TOC analysis were taken during carbon adsorption and ozonation testing.

TABLE 16. ASSAYS AND METHODS EMPLOYED DURING EXPERIMENTAL PROGRAM

Constituent	Assay Method	Reference
BOD	5 Day Incubation, Electrode	SM 219,218F*
COD	Dichromate Reflux	SM 220, EPA p. 21†
Color	Visual Comparison	SM 118
Conductivity	Meter Reading	SM 154
Iron	Atomic Absorption	SM 129, EPA p. 78
Lead	Atomic Absorption	SM 129
Oil and Grease (Freon Extractibles)	Separatory Funnel Extraction	SM 137, EPA p. 229
pH	Meter Reading	Manufacturer's Manual
Surfactants (Anionic)††	Colorimetric	SM 159A
Suspended Solids	Glass Fiber Filtration	SM 148C, SM 224C
TOC	Combustion-Methane Detection	EPA p. 236
Total Dissolved Solids	Glass Fiber Filtration	SM 148B
Turbidity	Meter Reading	SM 163A

* SM 101 (etc.) referes to procedure number in "Standard Methods for the Examination of Water and Wastewater", 13th Edition, APHA.

† EPA refers to "Manual of Methods for Chemical Analysis of Water and Wastes", U.S.E.P.A., 1974.

†† Positive interference may occur due to presence of chlorides in wastewater sample.

SECTION 6

EXPERIMENTAL RESULTS AND DISCUSSION

TEST PLAN

A flow chart of the unit operations through which each of the six synthetic rubber manufacturing wastewaters was processed is given in Figure 15. The raw wastewaters from each manufacturing process received ultrafiltration pretreatment, while the secondary effluents from the crumb rubber plants received dual-media depth filtration pretreatment. Depth filtration was also evaluated for the raw solution crumb and raw latex streams since they contained relatively low suspended solids loading (<150 ppm). However, due to poor performance during these tests (see below), neither of these two depth-filter effluents was processed further. The in-process latex wastewater was concentrated by ultrafiltration for possible reuse applications.

The principal treatment unit processes were carbon adsorption, reverse osmosis and ozonation. The two secondary treated waste streams pretreated by depth filtration were further processed by activated carbon adsorption to evaluate the BATEA treatment proposal. Carbon adsorption testing was also conducted with raw emulsion crumb, raw solution crumb, and in-process latex ultrafiltrates. Reverse osmosis testing was performed with the raw emulsion crumb, raw solution crumb, and in-process latex ultrafiltrates as well as with the secondary emulsion crumb depth filter effluent. Carbon adsorption and reverse osmosis tests were performed on identical streams in three cases and on similar streams in a fourth instance to comparatively evaluate the two processes. Treatment by ozonation, as a principal treatment process, was limited to the raw crumb rubber ultrafiltrate since, following these tests, it was concluded that the economics of ozonation as a principal treatment process are prohibitive.

The use of ozonation for posttreatment was investigated with the raw emulsion crumb reverse osmosis permeate and carbon column effluent, the raw solution crumb carbon column effluent, and the secondary treated emulsion crumb carbon column effluent.

The reverse osmosis process was highly effective in removing organics from the raw emulsion crumb waste; therefore, ozonation posttreatment would not be necessary. Thus, the results of the ozonation tests with this reverse osmosis permeate are not of direct importance, but may, nevertheless,

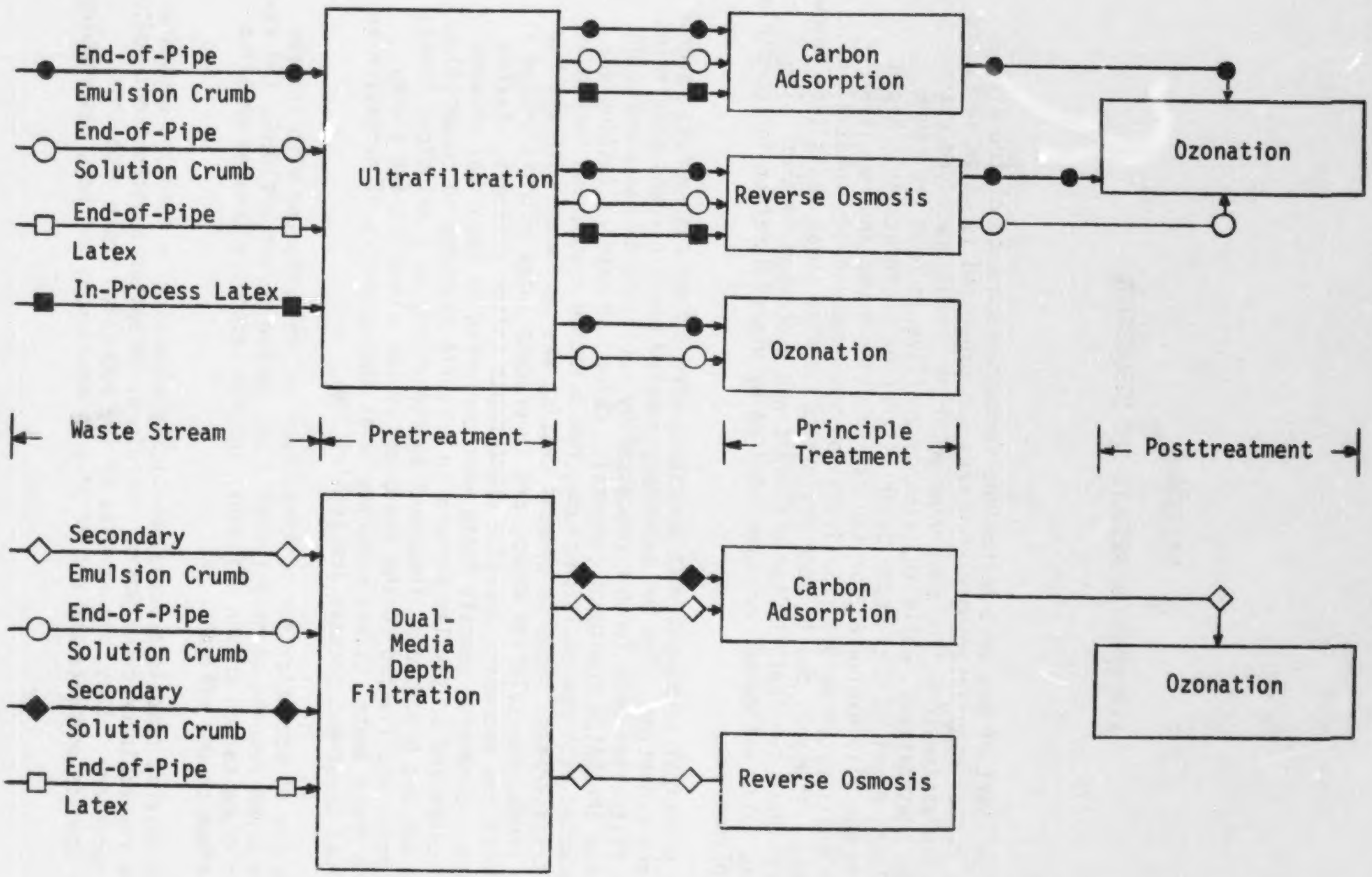

Figure 15. Flow chart of unit operations through which each synthetic rubber manufacturing wastewater was processed.

give an indication of the effects of operating parameters on the rate of ozonation of organics in emulsion crumb wastes.

Posttreatment of the raw solution crumb reverse osmosis permeate and the secondary solution crumb carbon column effluent was not warranted since BATEA standards were met by the principal treatment processes. Ozonation of the raw latex wastewater was precluded because of pretreatment processing difficulties discussed below.

The treatment of each wastewater type is discussed separately in the following sections. The test results for the alternative unit processes are presented in the order in which treatment would normally occur; i.e., pretreatment, principal treatment, posttreatment. For the secondary treated wastewaters, the proposed BATEA treatment processes of depth filtration and carbon adsorption are discussed jointly.

EXPERIMENTAL RESULTS FOR IN-PROCESS LATEX WASHDOWN WATERS*

Introduction

As discussed previously, ultrafiltration is best suited to the treatment of wastewater streams containing relatively high levels of suspended solids. Latex washdown waters (LWW) are highly laden with latex particles and are ideally suited to treatment by ultrafiltration. Such treatment would result in the recovery of latex which would otherwise be lost. The application of ultrafiltration for in-process latex wastewater treatment has been studied by Abcor, Inc. independent of this contract. Many of the ultrafiltration concentrates produced by treatment of in-process streams contain latex solids concentrations in excess of 40% and have been found quite suitable for recycle and reuse. Ultrafiltration has been shown to exhibit >95% reduction in both total solids and TOC for these streams, and the ultrafiltrates produced were found to be free of suspended solids.

In the following section, test data obtained with latex washdown wastewaters from a single plant will be presented. Ultrafiltration system performance during both laboratory and in-plant pilot testing are discussed, along with carbon isotherm and reverse osmosis experimentation with various LWW ultrafiltrates.

Laboratory Ultrafiltration Testing: Membrane Flux Characteristics

Ultrafiltration membranes generally show complete rejection of suspended matter regardless of the levels of operating variables. In contrast, membrane flux is significantly affected by the choice of these same operating parameters. Therefore, in the evaluation of ultrafiltration for treatment of synthetic rubber manufacturing wastewaters, primary emphasis has been placed on determining the dependence of membrane flux on process variables.

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*The data presented in this section were derived from laboratory and field tests conducted by the Operations Division of Abcor, Inc.

Four latex washdown wastewaters considered typical of the effluent streams requiring treatment at one SBR plant were tested. The streams contained latex concentrations of 17.5%, 11.4%, 3.6%, and 0.6%.

Abcor, Inc. Type HFM membranes have been determined in previous tests (12) to be a preferred membrane type for processing of washdown wastewaters. Therefore, only this type of membrane was used in the tests described below. Also, only tubular membrane modules were evaluated since alternative geometries are subject to plugging by coagulated latex and would be significantly more difficult to clean should membrane fouling occur.

The following sections describe test data, including the dependence of membrane flux on the important operating variables and membrane removal efficiencies for contaminants of concern.

Dependence of Membrane Flux on Feed Concentration Level--

Batch concentration tests were conducted with all four latex washdown wastewater streams at the following operating conditions:

Feed Circulation Rate	7.9 - 8.4 m^3/hr
Membrane Inlet Pressure	3.45 bar
Feed Temperature	50°C

These tests determined how membrane flux varied with both the initial latex concentration and the degree of volumetric concentration achieved. Figure 16 presents the data on membrane flux as a function of concentration level. Also shown in Figure 16 is the flux for the 0.6% latex sample to which a proprietary dispersant had been added (0.4%, based on the latex weight). This dispersant was added to reduce membrane fouling and increase the flux.

As observed in Figure 16, membrane flux for all LWW streams decreased as the solids concentration of the feed increased. The initial flux for the 0.6% latex sample without dispersant addition was 3.84 m^3/m^2-day (96 gfd). This is somewhat lower than would have been expected on the basis of the 3.98 m^3/m^2-day (99.5 gfd) initial flux for the 3.4% sample. Addition of dispersant to the 0.6% sample (hexagons in Figure 16) increased the initial flux to 4.4 m^3/m^2-day (111 gfd). This higher membrane flux was apparently the result of increased latex stability.

At those points in Figure 16 where the latex concentrations in two samples reach equal values, the flux levels achieved are, for the most part, dissimilar. This is most likely the result of inherent differences in the feed samples.

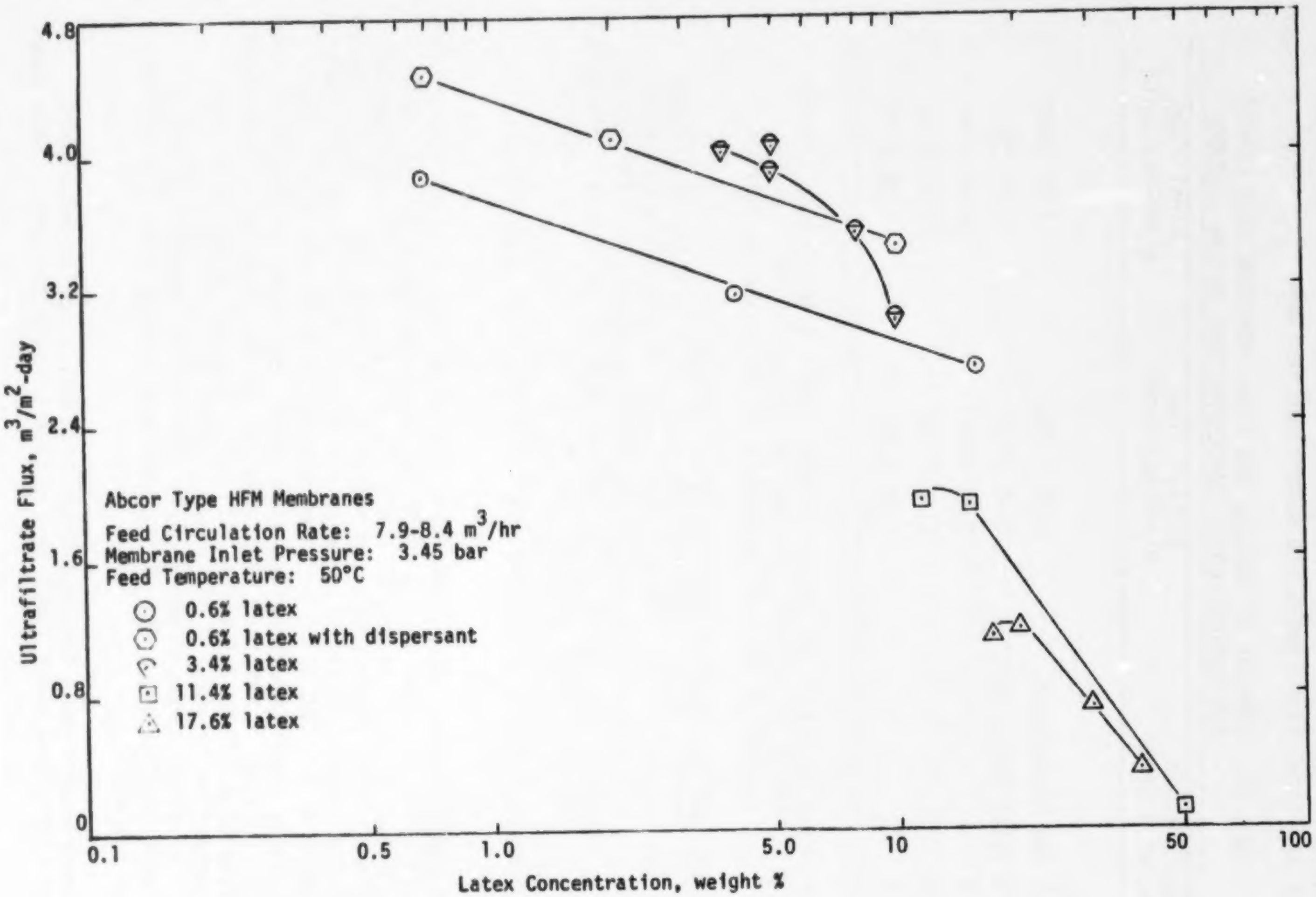

Figure 16. Ultrafiltration membrane flux vs. latex concentration for in-process latex wastes.

The range of concentrations achieved during these LWW-stream tests and the initial and final flux levels are summarized in Table 17.

TABLE 17. SUMMARY OF INITIAL AND FINAL MEMBRANE FLUX LEVELS FOR VARIOUS LATEX CONCENTRATIONS IN LWW STREAMS

Concentration Range, wt % Latex from	to	Initial Flux, m^3/m^2-day (gfd)	Final Flux, m^3/m^2-day (gfd)
0.6	14.5 (no dispersant)	3.82 (96)	2.72 (68)
0.6	6.8 (with dispersant)	4.44 (111)	3.43 (86)
3.6	17.5	3.98 (100)	0.41 (10)
11.4	49.5	1.95 (49)	0.12 (3)
17.6	40.0	1.15 (29)	0.28 (7)

It is to be noted that even at membrane flux levels below 0.40 m^3/m^2-day (10 gfd) the economics of ultrafiltration for latex recovery can be favorable. The subject of process economics is discussed in Section 7.

Dependence of Membrane Flux on Feed Circulation Rate--

The circulation rate through the membranes is of primary importance in determining membrane flux. It has been shown in numerous applications that as the circulation rate increases the flux increases, and therefore, the required membrane area for a given system capacity decreases. However, at higher flow rates a larger pumping system and more power are required. The selection of the optimum circulation rate is determined by a cost analysis which appropriately balances membrane costs and pump and power costs.

Batch concentration experiments were conducted with a 17.5% solids LWW sample at circulation rates of 5.2 m^3/hr (23 gpm) and 8.4 m^3/hr (37 gpm). Feed circulation rates in excess of 8.4 m^3/hr (37 gpm) are not recommended with latex containing feeds since agglomeration of latex particles can result from excessive shear. During both batch concentrations, the membrane inlet pressure was 3.45 bar (50 psig) and the feed temperature was 50°C. The results of these batch concentration experiments are shown in Figure 17. A substantial increase in membrane flux occurred as the feed circulation rate was increased from 5.2 to 8.4 m^3/hr. In fact, the membrane flux at any given concentration is about 2 1/2 times greater at 8.4 m^3/hr than at 5.2 m^3/hr. In other words, a tubular ultrafiltration system operated at 8.4 m^3/hr will require about 40% of the membrane surface area of a system operated at 5.2 m^3/hr.

The power requirement for an ultrafiltration system is determined almost entirely by the power input to the feed circulation pump. This power

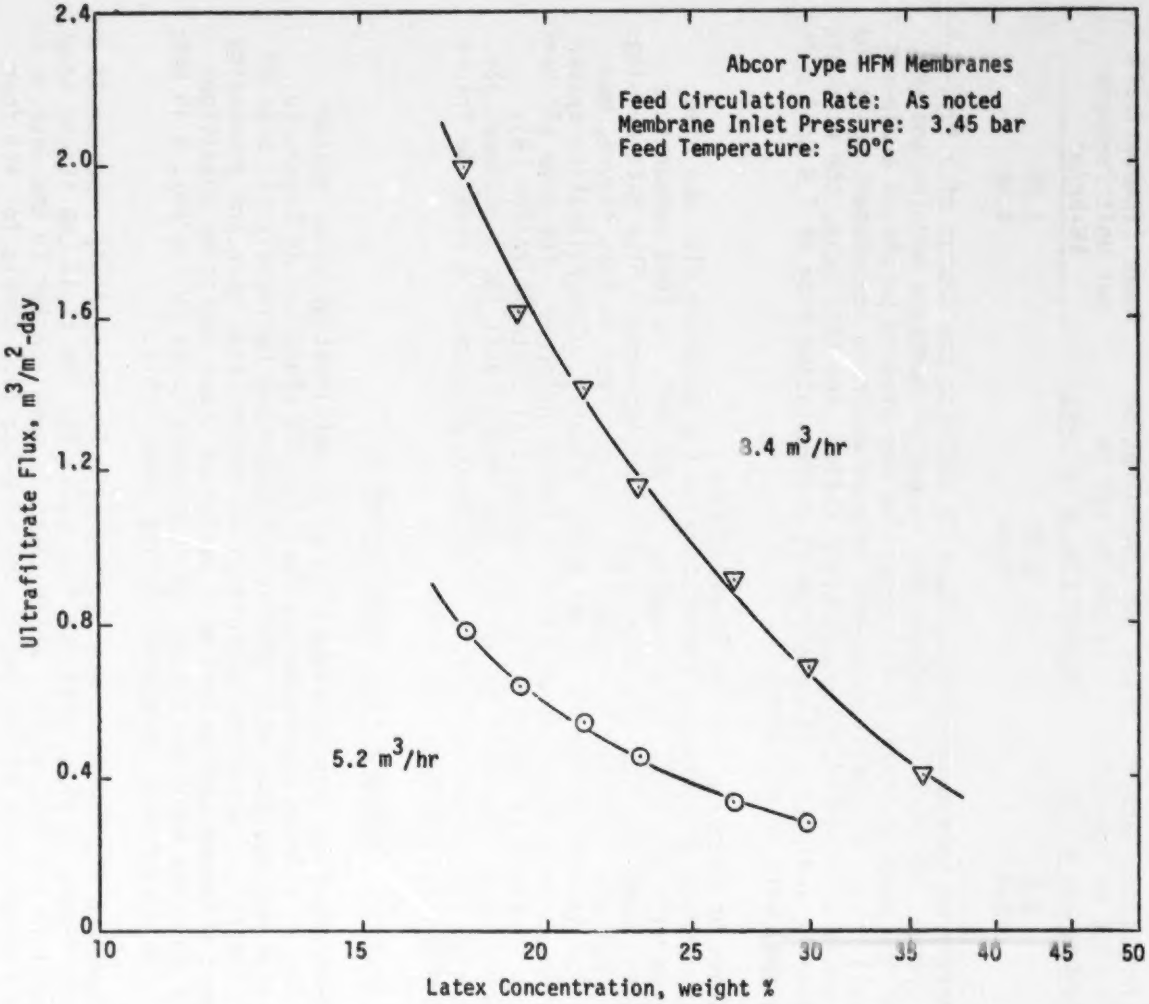

Figure 17. Ultrafiltration membrane flux as a function of feed circulation rate for in-process latex wastes.

input is directly proportional to the product of the circulation rate through, and the pressure drop across, the membrane system. The theoretical power requirements at each feed circulation rate are summarized below.

Circulation Rate in 25.4 mm Tubular Membranes, m^3/hr	Average Membrane Flux for Concentration to 30% Solids in Concentrate, m^3/m^2-day	Power (theoretical) per Unit Permeate kW-hr/m^3
5.2	0.57	3.26
8.4	1.44	4.92

Information of this nature can be used to optimize the design of a full-scale system. A trade-off between the number of membrane modules and the size of the pumping station will determine the minimum purchased equipment (capital) cost. A similar trade-off between membrane replacement costs and power costs will minimize the operating costs. For this case, the economic calculations indicate that operation at a circulation rate of 7.9 to 9 m^3/hr (35-40 gpm) will be preferred.

Dependence of Membrane Flux on Temperature--

The effect of operating temperature on the membrane flux was also evaluated with the 17.5% latex sample. In general, as feed temperature increases, membrane flux would be expected to increase. Flux data showing this effect are presented in Figure 18. As observed in this figure, membrane flux doubled between 27°C and 50°C. Clearly, ultrafiltration system operation at an elevated temperature is to be preferred. For some effluents, however, an elevated temperature may cause latex destabilization (9). Therefore, it is important to perform laboratory tests (at a minimum, jar tests) with each latex-containing waste to be processed in order to insure that destabilization does not occur.

Field Testing: Membrane Flux Characteristics

Membrane flux data obtained with an ultrafiltration pilot system operating at a latex manufacturing facility are presented in Figure 19. The system was equipped with tubular HFM membranes having a total area of 4.1 m^2 (44 ft^2). Batch concentrations of recirculated tank and processing equipment washdown wastewaters were performed under operating conditions similar to those employed during the laboratory tests (9.1 m^3/hr, 3.45 bar, 52°C). No dispersants were added during these tests.

Membrane flux versus concentration data for three field experiments are shown in Figure 19 along with the flux curve for the 11.4% LWW stream sample processed in the laboratory. While there is some scatter in the data up to a feed concentration of 30% latex, the membrane flux levels for all four experiments coincide at ~1 m^3/m^2-day (25 gfd) for a 30% solids concentration. Above this concentration level, the data are quite consistent. From these data an average design flux of 0.8 m^3/m^2-day (20 gfd) can be assumed for concentration of a 10% to 20% latex washdown wastewater stream

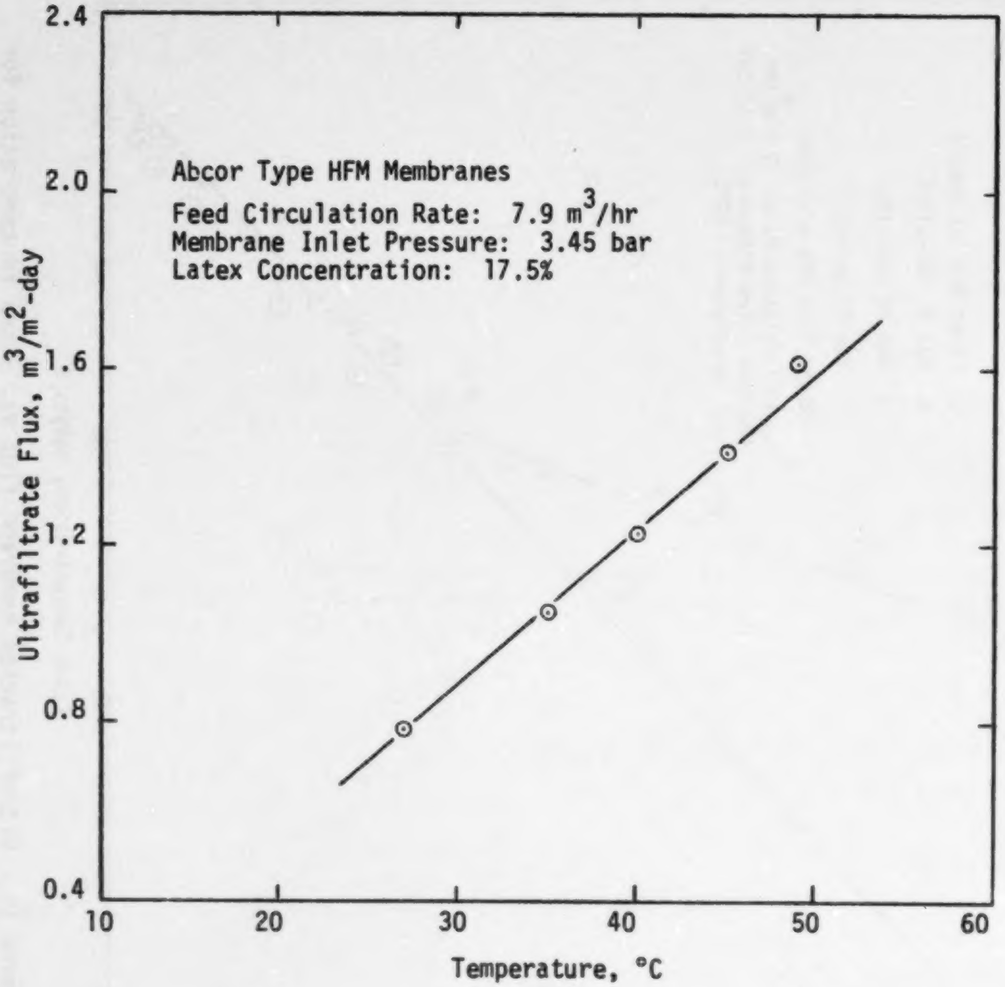

Figure 18. Ultrafiltration membrane flux as a function of operating temperature for in-process latex wastes.

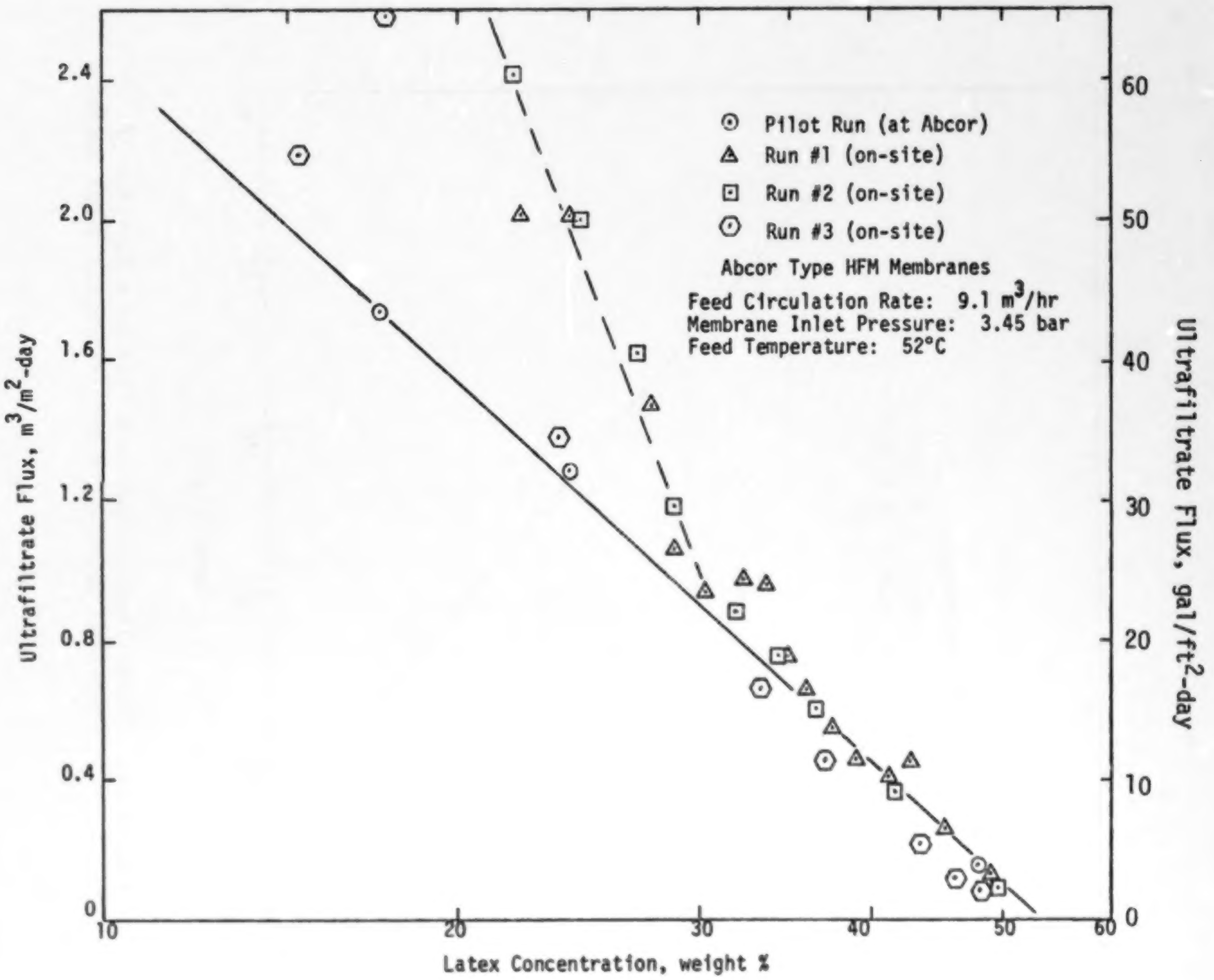

Figure 19. Ultrafiltration membrane flux vs. latex concentration for on-site pilot tests with in-process latex waste.

to a 40% to 50% solids level.

The flux levels for the field tests were higher than the laboratory test results below feed concentration of 30% solids. It is hypothesized that this may be due to improved latex stability resulting from reduced handling and immediate processing of samples in the on-site experiments.

Laboratory and Field Testing: Ultrafiltration Membrane Removal Efficiency Characteristics

Feed, concentrate, and composite ultrafiltrate samples from the 3.6% latex stream processed during the laboratory tests were analyzed for BOD_5, COD, and TOC. The results of these analyses are given in Table 18. From these data, it can be seen that the latex solids are the main contributor to the wastewater organic loading. In full-scale operation, the ultrafiltrate stream from washdown wastewater processing would be a portion (estimated at 70% to 90%) of the plant effluent. Therefore, while the composite ultrafiltrate does not meet either BPCTCA standard of 500 mg/ℓ COD or 25 mg/ℓ BOD_5, it reduces the contaminant levels substantially and may combine with the remaining plant waste stream to provide a total effluent of BPCTCA quality.

TABLE 18. ANALYTICAL DATA FROM LABORATORY ULTRAFILTRATION OF 3.6% LATEX LWW STREAM

Assay	Initial Feed (3.6% Latex)	Concentrate (10.3% Latex)	Composite Ultrafiltrate	Removal Efficiency, %
BOD_5 (mg/ℓ)	1,400	1,600	230	83.6
COD (mg/ℓ)	99,200	372,000	775	99.2
TOC (mg/ℓ)	23,800	86,600	222	94.9

Grab samples of concentrated washdown wastewater and ultrafiltrate were collected during the first field experiment. The analytical results for these samples are presented in Table 19. The assays performed with the concentrate were limited due to the ease with which the latex was coagulated by certain analytical procedures. The TOC and COD levels of the ultrafiltrate, 1620 mg/ℓ and 4020 mg/ℓ, respectively, reflect the high degree of concentration achieved (40% solids). Although an initial feed sample was not analyzed, high removals for BOD_5, COD, TOC, solids, and color are evident.

TABLE 19. ANALYTICAL DATA FROM ON-SITE ULTRAFILTRATION OF LWW STREAM

Assay	Final Ultrafiltration Concentrate	Composite Ultrafiltrate
% Solids	39.9	0.60
BOD_5 (mg/ℓ)	3,400	50
COD (mg/ℓ)	1,180,000	4,020
TOC (mg/ℓ)	---------	1,620
Suspended Solids (mg/ℓ)	---------	< 4
Surfactant (mg/ℓ)	---------	206
Iron (mg/ℓ)	---------	4.1
Lead (mg/ℓ)	---------	< 1.0
Color (units)	750,000	70

Additional Treatment of LWW Ultrafiltrates

Reverse Osmosis--

Following ultrafiltration of the 3.6% latex wastewater sample, the composite ultrafiltrate was processed through a duPont B-9 permeator. This laboratory test focused on membrane solute rejection. The composite ultrafiltrate (reverse osmosis feed) and composite reverse osmosis permeate analyses are tabulated below along with a partial listing of the BATEA effluent guidelines.

Assay	Reverse Osmosis Feed	Reverse Osmosis Permeate	BATEA
BOD_5 (mg/ℓ)	230	10	5
COD (mg/ℓ)	775	42	130
TOC (mg/ℓ)	222	8	---

The low BOD_5 and COD levels in the reverse osmosis permeate and the essentially complete removal of suspended solids by ultrafiltration suggest that a process train of ultrafiltration followed by reverse osmosis would produce an effluent from latex tank and tank car washdown wastewaters meeting BATEA standards.

The selection of the preferred reverse osmosis membrane and the optimum operating conditions requires further evaluation. Based on the ultrafiltrate dissolved solids content of 6020 mg/ℓ (following concentration of the LWW stream to a 40% solids level), a spiral-wound reverse osmosis module may be preferred. Spiral-wound modules have operating pressures of

41.4 bar (600 psig) as opposed to the B-9 module's 27.6 bar (400 psig) recommended pressure and are therefore better suited to process feeds with high solute concentrations.

Carbon Isotherm Data--

A seven-point carbon isotherm experiment was performed on an ultrafiltrate grab sample from the on-site pilot testing. The grab sample was collected when the latex concentration within the membrane loop reached 40% solids. The adsorption isotherm data are plotted in Figure 20. The slope of the isotherm is quite steep indicating poor adsorption of organics on the carbon. Even with a massive dose of carbon (5 gms/liter), only a 40% TOC reduction, from 1510 to 920 mg/ℓ, was achieved.

EXPERIMENTAL RESULTS FOR END-OF-PIPE LATEX WASTEWATER

Ultrafiltration Tests

Membrane Flux--

The initial ultrafiltration test with the raw latex (RLX) wastewater was performed with Abcor, Inc. Types HFD and HFM tubular membranes. System operating conditions were:

Mode of Operation	Batch
Circulation Flow Rate	6.81 m^3/hr
Inlet Pressure	3.45 bar
Temperature	38°C

Membrane flux is plotted as a function of time in Figure 21 for this batch concentration. A decrease in permeate flux with increasing time (and increasing feed concentration) is observed for both membrane types. The HFM membrane exhibited a higher average flux than the HFD membrane although after 0.7 hours both membrane types showed permeate outputs of <0.6 m^3/m^2-day (15 gfd). The batch concentration was discontinued (at 1.4 hours) when permeate flux fell below 0.4 m^3/m^2-day (10 gfd). At lower flux levels, the operation of any ultrafiltration system is generally considered to be uneconomical when the ultrafiltration concentrate is of no commercial value.

Several ultrafiltration experiments were conducted to evaluate various techniques for reducing the extent of membrane fouling by the end-of-pipe latex wastewater. First, two surfactants, Triton-X-100 and Tergitol S-15-9, were added to the wastewater in an attempt to stabilize the latices present. Next, the wastewater was allowed to settle before ultrafiltration treatment in order to reduce the amount of fouling material fed to the system. Finally, the feed circulation rate through the tubular assemblies was increased to reduce the boundary layer resistance at the membrane surface.

Directly following the batch concentration (i.e., no intermediate membrane cleaning), the ultrafiltration system was operated in a total recycle mode with 114 liters (30 gallons) of feed solution at a 1X volumetric

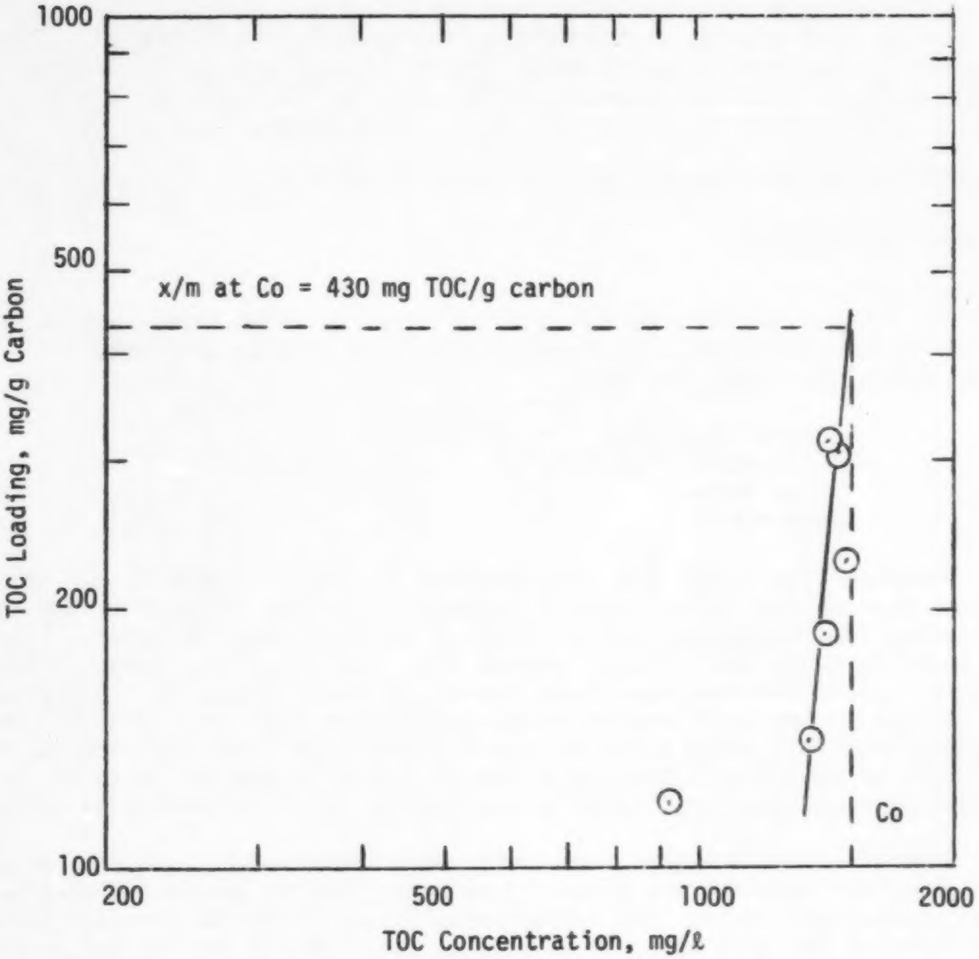

Figure 20. Equilibrium adsorption isotherm at 20°C for latex washdown water ultrafiltrate grab sample (latex concentration 40% solids at sampling).

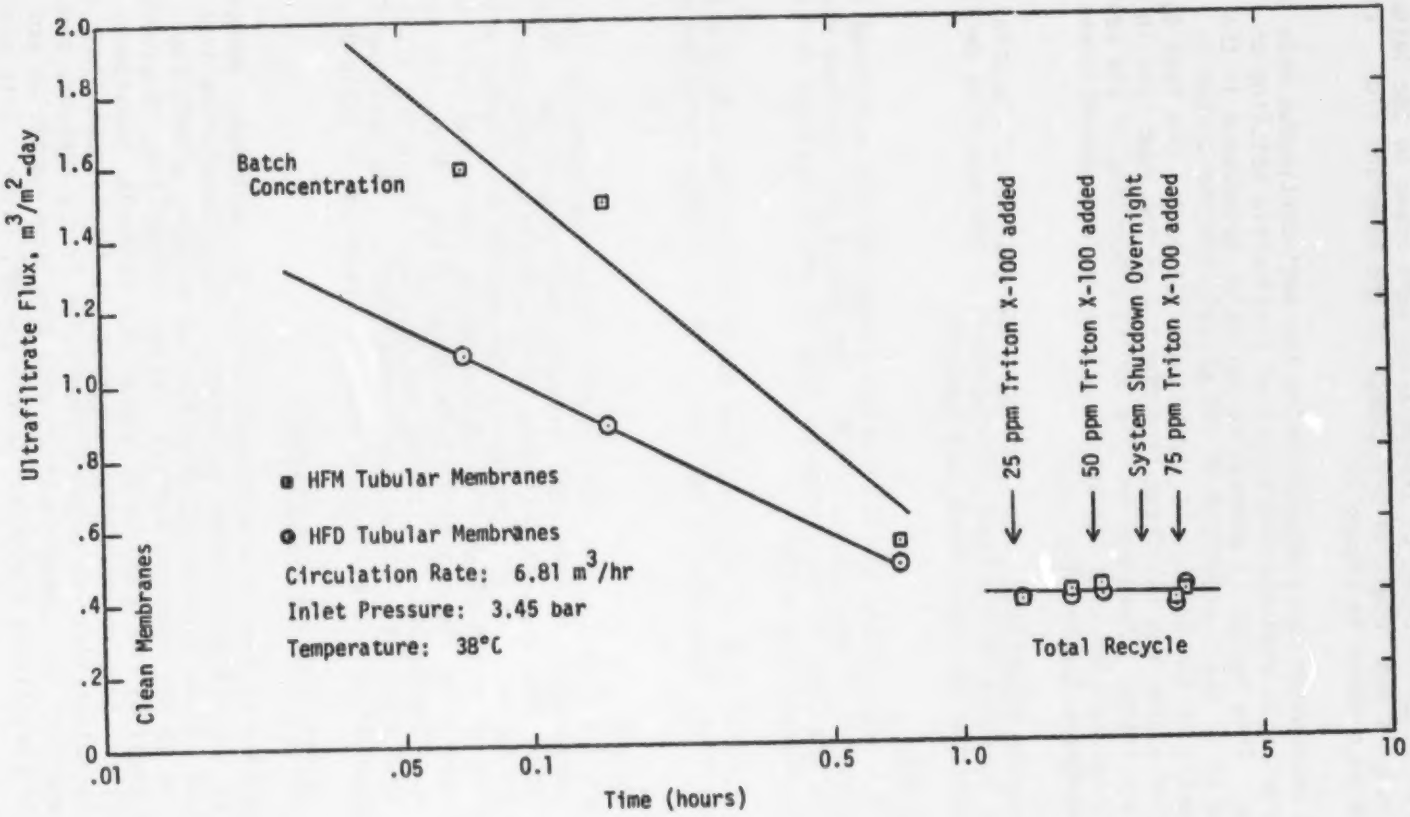

Figure 21. Ultrafiltration membrane flux vs. time for batch concentration of end-of-pipe latex wastewater and total recycle with dispersant addition.

concentration. Stepwise doses of Triton-X-100 were added to the latex wastewater, but did not result in any change in the membrane flux. These flux data are also shown in Figure 21.

The RLX wastewater was processed using the semi-continuous mode of operation in order to evaluate the effect of particulate settling on membrane flux. This method of processing maintains quiescence in the settling tank since the concentrate of the ultrafiltration system is returned directly to the suction of the circulation pump. The feed to the ultrafiltration system was withdrawn from the top of the feed tank in order to limit solids intake. Membrane fouling during processing of the settled feed was less severe than with the constantly mixed feed; nevertheless, substantial membrane fouling did occur.

Total recycle experiments involving both the addition of Tergitol S-15-9 and an increase in the feed circulation rate produced flux declines similar in magnitude to those shown in Figure 21.

Membrane Rejection--

For the RLX wastewater, the HFD and HFM membranes both exhibited TOC removal efficiencies of approximately 80%. The TOC of the raw feed was 320 mg/liter, while the TOCs of the permeates were 66 and 70 mg/liter for the HFM and HFD membranes, respectively.

The BOD_5 removal for the HFM membrane was also measured. At the time of sampling the feed, BOD_5 was 100 mg/liter, and a 53% BOD_5 reduction was obtained.

Membrane Flux Recovery--

Despite the rapid fouling of the ultrafiltration membranes by the end-of-pipe latex wastewater, no permanent membrane fouling occurred. This was determined by water flux measurements made after a modified cleaning procedure was performed. In this procedure, the system was flushed with a 0.5 wt % solution of "Ultra-Clean" for 10 minutes to remove the bulk fouling layer prior to beginning the standard cleaning operation. Also, the use of mechanical (i.e., "sponge-ball") cleaning was necessary following ultrafiltration of this end-of-pipe latex wastewater sample. The membrane flux recovery and accumulated operating time data are presented in Table 20.

Discussion of Ultrafiltration Test Results

The instability of the latices present in the RLX wastewater promoted rapid fouling of the ultrafiltration membranes. Latex coagulation into rubber crumb occurred on the coarse, prefiltering screens, within the system piping and on the membrane surface. Latex instability, in general, may be brought about by the presence of any of the following substances in the latex solution: bivalent metallic ions (e.g., calcium, magnesium, etc.), hydrogen ions (acidification) or organic impurities (e.g., acetone, benzene, etc.). These chemical substances interact with the latex particles and break down their stabilizing electrical double (outer) layer. This action

TABLE 20. FLUX RECOVERY AND ACCUMULATED OPERATING TIMES FOR ULTRAFILTRATION MEMBRANE OPERATED ON END-OF-PIPE SBR WASTEWATER

Membrane Type/Configuration	Designation	Accumulated Exposure Time (hours)	Water Flux before "spongeball" m^3/m^2 day	Water Flux after "spongeball" m^3/m^2 day	Comments
HFD/Tubular	D1 - D3	135	4.72	5.0	At completion of raw emulsion crumb wastewater testing
	D4 - D7	0	-	9.64	New membranes - raw latex wastewater testing
		4	-	10.48	
		5.3	-	-	Replaced during run, data not available
HFM/Tubular	M1 - M3	135	15.84	17.20	At completion of raw emulsion crumb wastewater testing
	M4 - M11	76	7.96	11.08	At completion of raw emulsion crumb wastewater testing
	M4 - M7	80	-	8.24	Raw latex wastewater testing
		84	4.72	8.08	
		90	0.72	5.80	
		93	1.16	4.04	
	M8 - M11	78	11.2	14.24	Raw latex wastewater testing
		84	1.0	14.08	
		87	2.4	10.68	

lowers the particles' intermolecular potential energy barrier allowing flocculation and/or coagulation to proceed more readily.

The exact cause of the chemical instability of the end-of-pipe latex wastewater could not be determined, and the ultrafiltration tests were discontinued.

Dual-Media Depth Filtration Tests

Jar tests with the end-of-pipe latex wastewater indicate that significant latex flocculation takes place at pH 11.5. The RLX wastewater was therefore pH adjusted to induce flocculation and treated for suspended solids removal by dual-media depth filtration.

Filter Performance--

The 0.05 m diameter dual-media depth filter was used to determine both filtrate turbidity and column headloss versus process time for treatment of RLX wastewater flocculated by pH adjustment. As shown in Figure 22, the filtrate turbidity decreased rapidly to < 2 NTU, and except for a minor upset following overnight shutdown, remained below 2 NTU for the 9 hour processing period.

The headloss through the column rose steadily reaching 1.7 bar (25 psig) at system shutdown. For gravity filters, allowable headlosses generally are below 0.28 bar (4 psig) (6). Use of a gravity filter in field applications would necessitate media regeneration (backflushing) after 3 to 4 hours of operation (see Figure 22). Since the lower limit on filter run lengths is 6 to 8 hours (6), pressure filters would be favored for dual-media depth filtration of end-of-pipe latex wastewaters.

The excellent turbidity removal exhibited by the 0.05 m diameter column warranted further depth filtration testing with the end-of-pipe latex wastewater. The pH of 0.8 m^3 (210 gal) of latex process wastewater was raised, and the flocculated solution was processed through the 0.23 m diameter column. An initial filtrate turbidity of 60 NTU was observed. This amounts to an order-of-magnitude increase over the initial turbidity of the effluent from the 0.05 m diameter column. Since the filtrate turbidity remained above 15 NTU throughout the run, it is suspected that channeling occurred within the larger column. Also, a higher column headloss during filtration indicated that solids caking on the filter surface proceeded at almost twice the rate observed for the smaller diameter column.

The relatively high turbidity of the composite depth filter effluent, 34 NTU, precluded use of reverse osmosis or carbon adsorption as the next process step. In order to make the depth filter effluent more amenable to further treatment, it was reprocessed through the 0.23 m diameter column. No backflushing was performed between the two runs. Within an hour the filtrate turbidity and column headloss had stabilized at 6.8 NTU and 0.9 bar (13 psig), respectively. Although an 80% turbidity reduction resulted

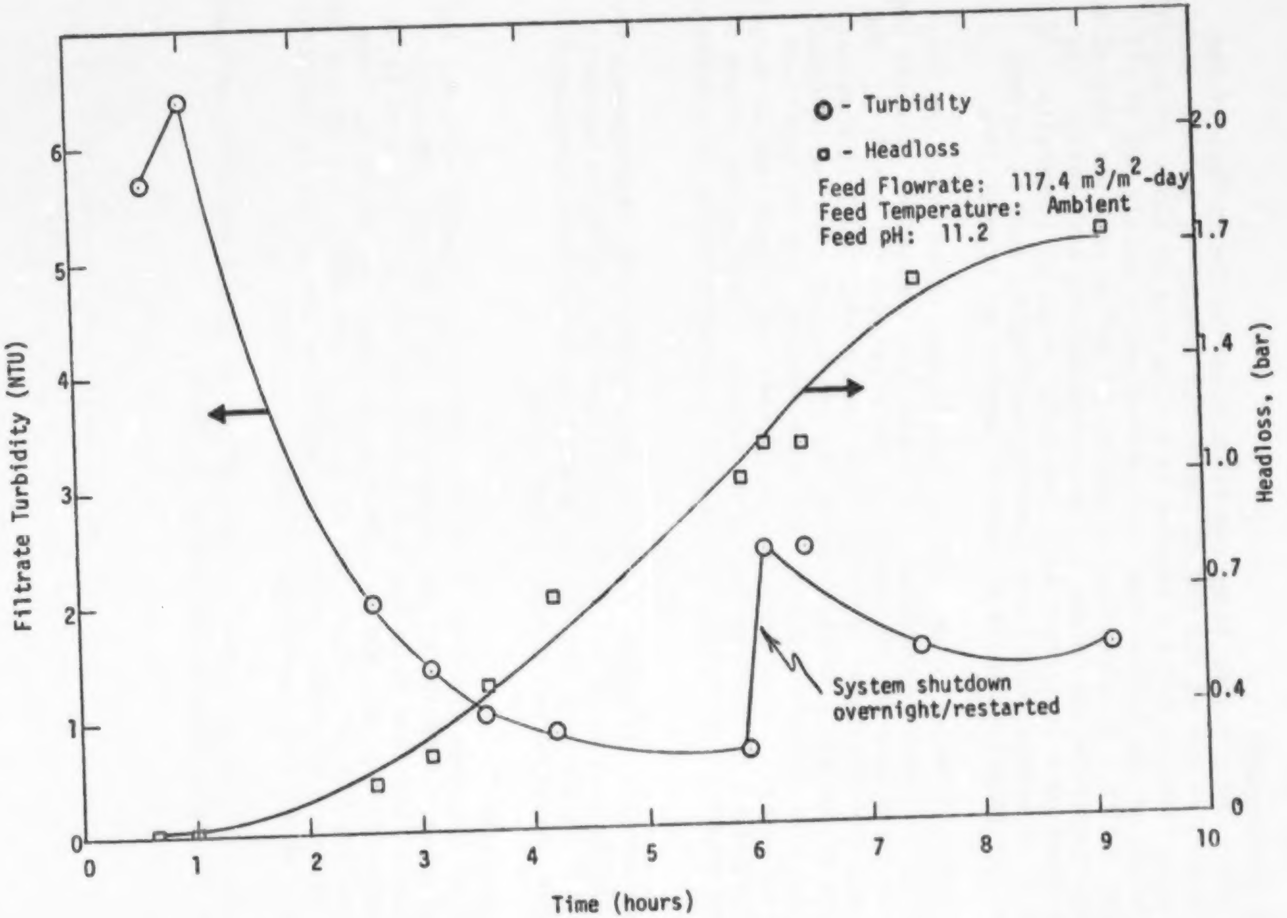

Figure 22. Filtrate turbidity and column headloss vs. time for dual-media depth filtration of end-of-pipe latex process wastewater; 0.05 m diameter column.

from the reprocessing step, the dual-media depth filter effluent was still too turbid for subsequent reverse osmosis and carbon column processing.

Backflush Requirements--

A 0.006 m thick solids layer was found caked on the surface of the 0.05 m diameter column at the end of the 9 hour processing period. Backflushing with filtrate for 4.5 minutes at a flow rate of 880 m^3/m^2-day (15 gpm/ft^2) broke up the solids layer and removed approximately 90% of all accumulated solids. An additional 6 minutes of upflow wash was applied to completely regenerate the column before processing the next waste. The backflush times were consistent with industrial practice (generally < 10 min), and if necessary, auxiliary cleaning techniques, such as surface washing or air scouring, could be used to improve bed regeneration.

The 0.23 m diameter column was not backflushed until after the first-pass filtrate had been reprocessed. Filtrate from the second pass was used to backwash the column for 19 minutes at 646 m^3/m^2-day (11 gpm/ft^2). The backwash was then continued with tap water for an additional 19 minutes. Examination of the media surface showed the anthracite layer to be caked with solids. The upper 0.013 m of coal were removed, and the backflush operation continued. Twice more the upflow wash was interrupted to manually remove accumulated solids from the media surface. Clearly, the extent of backwashing required to regenerate the 0.23 m-diameter column is unacceptable.

A considerable difference exists in the backflushing requirements for the two columns. Latex destabilization, similar to problems encountered during ultrafiltration of the RLX wastewater may have caused coagulation of latex within the media bed of the larger column.

Contaminant Removal--

Table 21 presents the feed, filtrate, and backwash water analyses for dual-media depth filtration of the end-of-pipe latex process wastewater. Flocculation of the feed solution lowered the TOC and COD levels by 62.5% and 32%, respectively, but had no effect on the feed BOD_5 of 66 mg/liter. Filtrate quality was very consistent in terms of BOD_5, COD, and TOC for the two runs; however, suspended solids (and therefore turbidity) in the larger diameter column filtrate were significantly increased.

The depth filter effluent is compared to the BPCTCA and BATEA effluent guidelines for latex process wastewater in Table 22.

TABLE 21. CONTAMINANT ANALYSES FOR DUAL-MEDIA DEPTH FILTRATION OF END-OF-PIPE LATEX PROCESS WASTEWATER

Contaminant	Initial Feed	Flocculated Feed	0.05m Diameter Column Backwash	0.23m Diameter Column Composite Filtrate	0.05m Diameter Column Composite Filtrate
Total Dissolved Solids (mg/l)	865	1120	770	1050	806
Suspended Solids (mg/l)	133	312	646	19	< 4
Oil and Grease (mg/l)	41	23	76	< 4	7
TOC (mg/l)	320	120	180	80	80
COD (mg/l)	1350	916	1810	240	239
BOD_5 (mg/l)	66	66	175	65	80
Surfactants (mg/l)	2.11	3.8	6	1.43	1.4
Iron (mg/l)	< 1	1.2	3.3	< 1	< 1
Lead (mg/l)	< 1	< 1	< 1	< 1	< 1
Color (units)	700	200	400	20	10
Turbidity (NTU)	590	-	-	34	2.1
pH	5.2	9.7/11.3	11.0	9.4	11.2
Conductivity (μmhos/cm)	1000	-	780	1550	1200

TABLE 22. COMPARISON OF DEPTH FILTER EFFLUENT WITH EFFLUENT GUIDELINES FOR LATEX MANUFACTURING WASTES

Assay	0.05 m Diameter Column Filtrate	0.23 m Diameter Column Filtrate	BPCTCA	BATEA
COD (mg/ℓ)	239	240	500	130
BOD_5 (mg/ℓ)	80	65	25	5
Suspended Solids (mg/ℓ)	<4	19	40	10
Oil and Grease (mg/ℓ)	7	<4	10	5

The BPCTCA guidelines were met in both instances for all analyses except BOD_5. Only the suspended solids analysis for the smaller column filtrate and the oil and grease analysis for the 0.23 m diameter column filtrate met the BATEA guidelines.

Activated Carbon Adsorption Tests

Because of latex coagulation during dual-media depth filtration of the RLX wastewaters, meaningful carbon-adsorption column tests could not be conducted as originally planned. Therefore, the viability of the proposed BATEA treatment processes for this waste has not been demonstrated during this program. It is clear, however, that a stable waste stream is a prerequisite for applying the proposed BATEA processes and that the waste and/or experimental conditions employed did not satisfy this prerequisite. Since only one RLX waste stream was evaluated during these tests, restraint should be exercised in the generalization of these results.

EXPERIMENTAL RESULTS FOR END-OF-PIPE EMULSION CRUMB WASTEWATER

Ultrafiltration Tests

Selection of Preferred Membrane--

Two preliminary UF total recycle experiments were conducted with types HFA, HFD, and HFM membranes. The two tests were identical, except for the addition of Triton X-100 non-ionic surfactant during the second test. The flux and rejection characteristics of the three membrane types during these experiments are presented in Appendix A.

Average flux levels of 2.4 to 4 m^3/m^2-day (60 to 100 gfd) were observed for the three membrane types during the first 20 hours of each experiment. After 20 hours, in both tests, a rapid flux decline was observed for all membranes. The apparent cause of this decline was latex instability which resulted in membrane fouling.

In summary, the HFM membrane type was chosen for further testing with the REC wastewater based on the following considerations.

1. The average flux of the HFM membrane for the preliminary total recycle experiments equaled or exceeded the average flux of the HFA and HFD membranes.
2. The HFM membrane exhibited the highest TOC rejection of the three membrane types.
3. The HFM membrane is the most resistant to environmental attack of the three membrane types and is the only one which is not susceptible to attack by free-chlorine.
4. The flux recovery, after cleaning, of the HFM membrane was excellent as compared to moderate flux recoveries for both the HFA and HFD membranes (see below).

Membrane Flux--

Figure 23 gives the flux vs. time curves for the batch concentration of raw emulsion crumb wastewater to a volumetric feed concentration of 20X. During this test, the HFM membrane was evaluated in both the tubular and spiral-wound configurations which were operated in parallel. The spiral module contained a corrugated feed-side spacer which had 0.002 m (nominal) corrugations. The circulation flow rate was maintained at 6.8 m^3/hr (30 gpm) for the tubular module and 22.7 m^3/hr (100 gpm) for the spiral module. The membrane inlet pressure was 3.1 to 3.45 bar (45 to 50 psig) and the temperature was 38°C.

The flux for the tubular assembly was consistently greater than for the spiral module throughout the entire batch concentration. However, the short duration of the pumpdown acted in favor of the tubular configuration since water flux and initial flux values of spiral modules are generally lower than for tubular membrane assemblies. The data presented in Figure 23 indicate no gross particulate plugging of the channels in the feed-side spacer of the spiral-wound module. The average flux was 4.8 m^3/m^2-day (120 gfd) for the tubular assemblies and 3.6 m^3/m^2-day (90 gfd) for the spiral-wound module.

Total recycle experiments at 1X and 5X volumetric feed concentrations were performed with the tubular and spiral-wound HFM modules to further detail their flux characteristics with the REC wastewater and to provide data on membrane life during exposure to this waste stream. The flux vs. time data for these experiments are presented in Figure 24. The severe membrane fouling which was noted in the preliminary tests did not occur during these tests, indicating that slight changes may have occurred in the feed composition and/or characteristics.

The flux levels for the tubular membranes were higher during the test with the more concentrated waste suggesting that additional changes in waste composition occurred. The 5X concentration test was terminated after 20 hours due to failure of a mechanical seal in the main circulation pump while

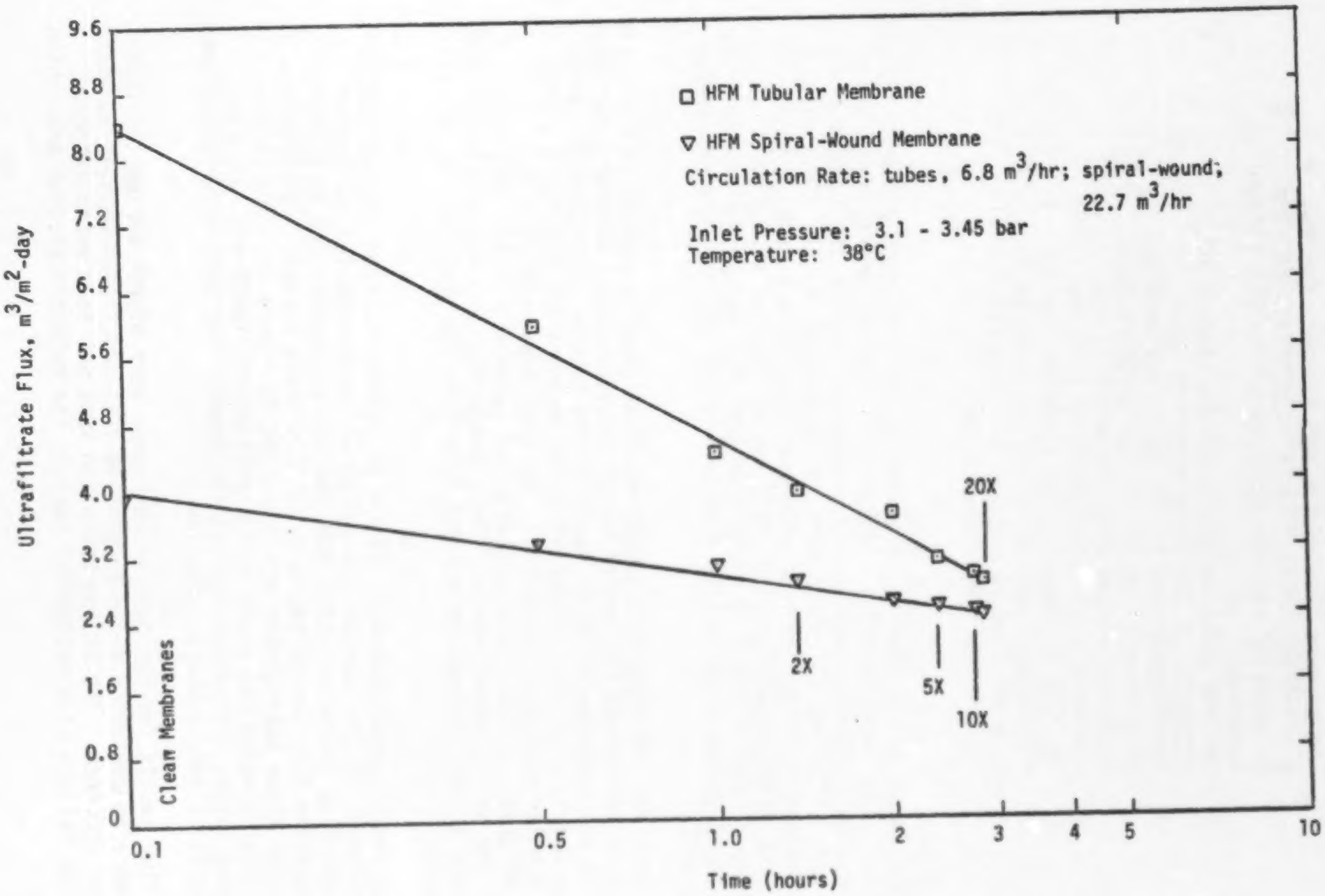

Figure 23. Ultrafiltration membrane flux vs. time for batch concentration of end-of-pipe emulsion crumb wastewater to a 20X feed volumetric concentration.

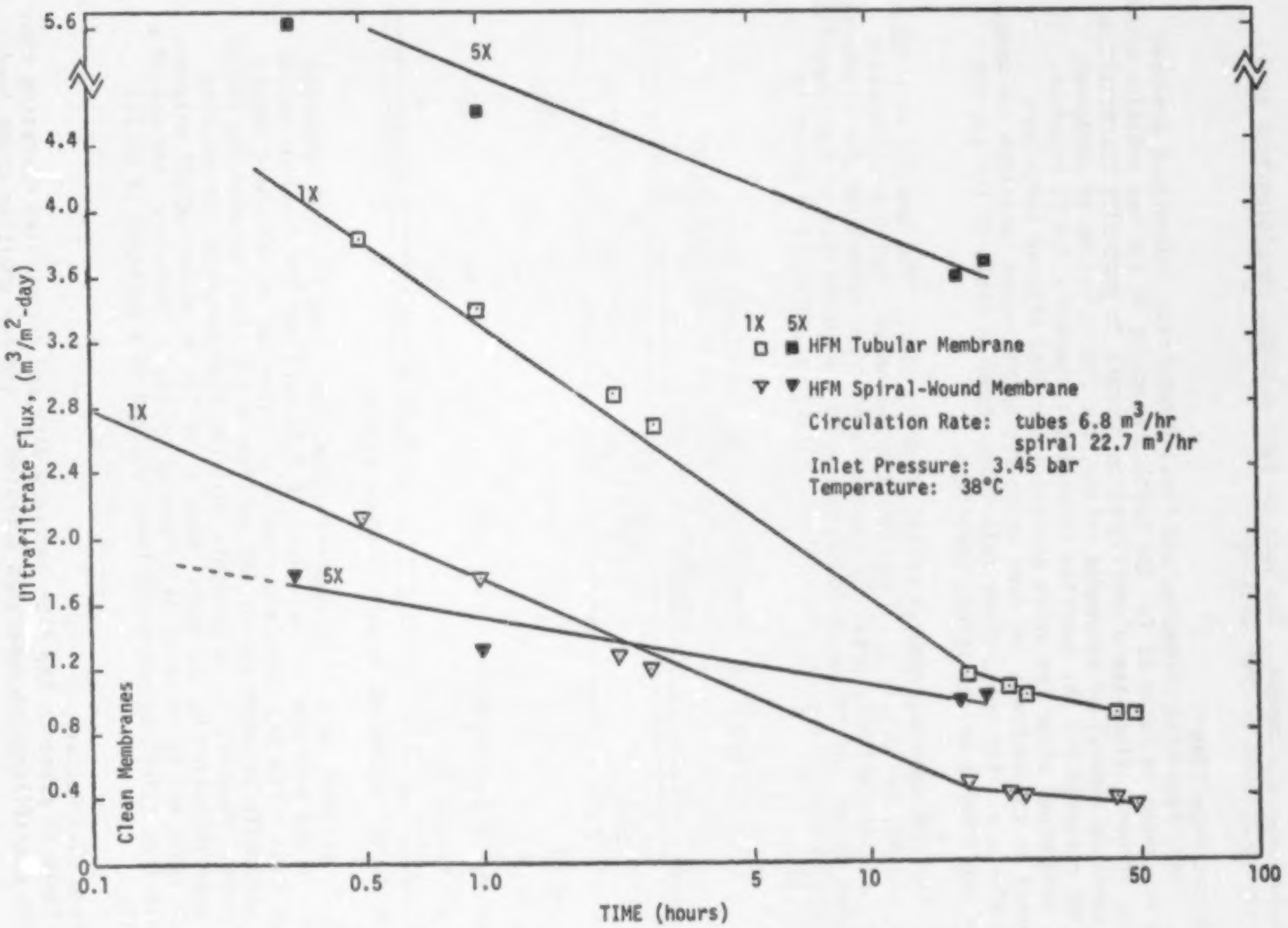

Figure 24. Ultrafiltration membrane flux vs. time for 1X and 5X feed concentrations of end of pipe emulsion crumb wastewater; tubular and spiral-wound membranes.

the test was unattended. The loss of feed solution resulting from seal leakage precluded further testing.

Membrane Rejection--

Feed, composite permeate, and final concentrate contaminant analyses are presented in Table 23 for the batch processing of the raw emulsion crumb waste stream. Since the ultrafiltration process is generally characterized by complete removal of suspended solids, the 75% rejection of suspended solids observed for the emulsion crumb waste concentration is atypical. It was determined after the batch concentration that pinhole leaks were present in the membrane lot from which the spiral-wound cartridge was made. Therefore, all the contaminant rejections shown in Table 23 reflect the poor performance of the spiral cartridge.

The HFM membrane removal efficiencies for BOD_5, TOC, and COD were 88%, 26%, and 9%, respectively. Thus, it does not appear that ultrafiltration alone can successfully treat the raw emulsion crumb wastewater for discharge to meet either the BPCTCA or BATEA standards. A comparison of the composite ultrafiltrate quality and the effluent guideline standards is given in Table 24.

TABLE 24. COMPARISON OF ULTRAFILTRATE WITH EFFLUENT GUIDELINES FOR EMULSION CRUMB MANUFACTURING WASTES

Assay	Composite Ultrafiltrate	BPCTCA	BATEA
COD (mg/ℓ)	830	500	130
BOD_5 (mg/ℓ)	12	25	5
Suspended Solids (mg/ℓ)	(48)[*]	40	10
Oil and Grease (mg/ℓ)	5	10	5

[*] Pinhole leak suspected in spiral-wound module.

If it is assumed, to a first approximation, that 1 mg/liter of suspended solids in the permeate is equivalent to 3.43 mg/liter COD (average solids composition = $(CH_2)n$), complete removal of suspended solids would result in a composite permeate COD of 665 mg/liter which still exceeds the BPCTCA guideline. However, it is possible that the high permeate COD resulted from poor rejection by the spiral module for low molecular-weight polymers (which would not be detected as suspended solids). Therefore, the use of a pinhole-free spiral module might have resulted in a permeate of BPCTCA quality.

Membrane Flux Recovery--

Table 25 presents the flux recovery data and accumulated operating time for the ultrafiltration membranes operated on the raw emulsion crumb feed.

TABLE 23. CONTAMINANT ANALYSIS FOR ULTRAFILTRATION OF END-OF-PIPE EMULSION CRUMB WASTEWATER

Contaminant	Feed	Final Concentrate*	Composite Permeate**	Rejection, %[†]
Total Dissolved Solids (mg/l)	30,140	30,420	30,480	-
Suspended Solids (mg/l)	191	1890	48	74.8
Oil and Grease (mg/l)	12	198	5	58.3
TOC (mg/l)	334	1830	246	26.3
COD (mg/l)	917	4340	830	9.5
BOD_5 (mg/l)	98	400	12	87.8
Surfactants (mg/l)	0.142	0.142	(0.34)	-
Iron (mg/l)	8.2	18	6.3	23.2
Lead (mg/l)	< 1	< 1	< 1	-
Color (units)	320	4000	120	62.5
Turbidity (NTU)	190	-	2.4	98.7
pH	5.7	-	6.5	-
Conductivity (μmhos/cm)	35,000	-	30,000	16.7

* Concentrate disposal methods were not evaluated during this program.

** Tubular and spiral-wound membranes, pinhole leak suspected in spiral-wound cartridge.

[†] Rejection, $R = \frac{\text{concentration of feed - concentration of composite permeate}}{\text{concentration of feed}} \times 100$

TABLE 25. FLUX RECOVERY AND ACCUMULATED OPERATING TIMES FOR ULTRAFILTRATION MEMBRANES OPERATED ON END-OF-PIPE EMULSION CRUMB WASTEWATER

Membrane Type/Configuration	Designation	Accumulated Exposure Time (hours)	Water Flux before "Spongeball" (m^3/m^2-day)	Water Flux after "Spongeball" (m^3/m^2-day)
HFA/Tubular	A1, A2	0	5.48	-
		94	5.16	5.60
		135	4.96	5.04
HFD/Tubular	D1, D2, D3	0	5.84	-
		94	7.40	10.0
		135	4.72	5.0
HFM/Tubular	M1, M2, M3	0	5.40	-
		94	12.16	17.84
		135	15.84	17.20
	M4-M11	0	10.44	-
		3	-	8.84
		52	-	8.56
		56	6.36	9.04
		76	7.96	11.08
HFM/Spiral-Wound	MS1	0	-	4.16
		3	-	4.16
		52	-	2.12
		56	-	2.52
		76	-	-*

* Following mechanical seal failure, no water flux taken to date

The increase in water flux to a level above the initial flux after exposure to the waste and cleaning is common, since the non-ionic surfactant in the cleaning solution improves the wetting of the membrane surface. Particulate plugging of the corrugated spacer channels during the total recycle experiments appears to have limited the spiral module flux recovery.

Reverse Osmosis Testing

Selection of Preferred Membrane--

Two preliminary total recycle experiments were performed to determine the preferred reverse osmosis membrane module for processing the emulsion crumb ultrafiltrate. In the first experiment, a spiral-wound cellulose acetate (CA) module and a hollow-fine-fiber B-9 module were operated in series with each other. In the second experiment, the CA module and a hollow-fine-fiber B-10 module were tested in series. The CA module was placed ahead of the B-9 or B-10 module in each case. The CA module is operated at lower conversion than either the B-9 or B-10 module, and hence, the concentrate from the CA module is only slightly more concentrated than the feed and provides a suitably representative feed stream for the second module in series. If a B-9 or B-10 high-conversion module was placed ahead of the CA module, a very concentrated and, therefore, unrepresentative feed stream would enter the CA module. Also, because of the differences in contaminant rejections, performance of the modules must be compared during total recycle tests. During a batch concentration experiment, the high rejection module would dominate permeate quality and consequently determine contaminant build-up (rejected species) in the feed.

The inlet pressure to the CA and B-9 permeators in the first experiment were 41.4 bar (600 psig) and 27.6 bar (400 psig), respectively. During the second experiment, the B-10 module had to be tested below the recommended operating pressure of 55.2 bar (800 psig) in deference to the CA module which has a maximum inlet pressure of 41.4 bar and was exposed to an inlet pressure of 38.6 bar (560 psig). The pH of the feed stream was maintained between pH 5 and pH 6 to remain within the pH limits of all modules tested.

Samples of the feed and reverse osmosis module permeates were taken after 1 hour and at the end of each run and analyzed for TOC. Average TOC removal efficiencies and product flow rates are summarized below:

Module	Average Productivity, m^3/day (gpm)	Average TOC Removal Efficiency, %
Cellulose Acetate	2.48 (0.45)	92.4
B-9	5.06 (0.92)	92.1
B-10	4.40 (0.80)	96.6

The B-10 hollow-fine-fiber module was selected for further testing with the emulsion crumb ultrafiltrate for two reasons. First, the B-10 exhibited the highest TOC rejection of the three modules tested. Secondly, the high dissolved solids content of the composite ultrafiltrate, 30,480 mg/ℓ, would result in high osmotic pressures. The B-10 module, with an operating pressure of 55.2 bar, is best suited to overcome the osmotic pressure build-up during the concentration process.

Module Productivity--

The B-10 permeate flow rate as a function of solute rejection during the batch concentration of the REC ultrafiltrate is shown in Figure 25. The plotted relationship between module productivity and membrane rejection is derived from reverse osmosis theory. The data in Figure 25 fall on a straight line (as predicted by theory) indicating that osmotic pressure, rather than membrane fouling, was the cause of the decline in B-10 productivity during batch concentration. The productivity of the B-10 module decreased from 6.67 m^3/day (1.21 gpm) initially to 2.48 m^3/day (0.45 gpm) at a 2X volumetric feed concentration to 0.11 m^3/day (0.02 gpm) at a 2.6X feed concentration.

The experimental goal of concentrating to a 10-20X concentration (90% to 95% conversion) could not be met due to the low water productivity at the 2.6X concentration. High water recoveries, for streams with no concentrate reuse value, are generally required if process economics are to be favorable.

The history of the reverse osmosis module salt rejections during processing of the emulsion crumb ultrafiltrate are presented in Table 26. Operating hours on the ultrafiltrate stream were accumulated by performing total recycle life tests at 1X and 2X volumetric feed concentrations with both the CA and B-10 modules. The high osmotic pressures which develop after a 2X concentration limited the feed concentrations tested. No membrane degradation due to compaction or environmental attack was noted for any of the modules tested.

Module Rejection--

Feed, initial permeate, composite permeate, and final concentrate analyses for the batch concentration of the REC ultrafiltrate to a volumetric feed concentration of 2.6X are presented in Table 27. The analyses which are common to the Development Document guidelines are compared in Table 28, below.

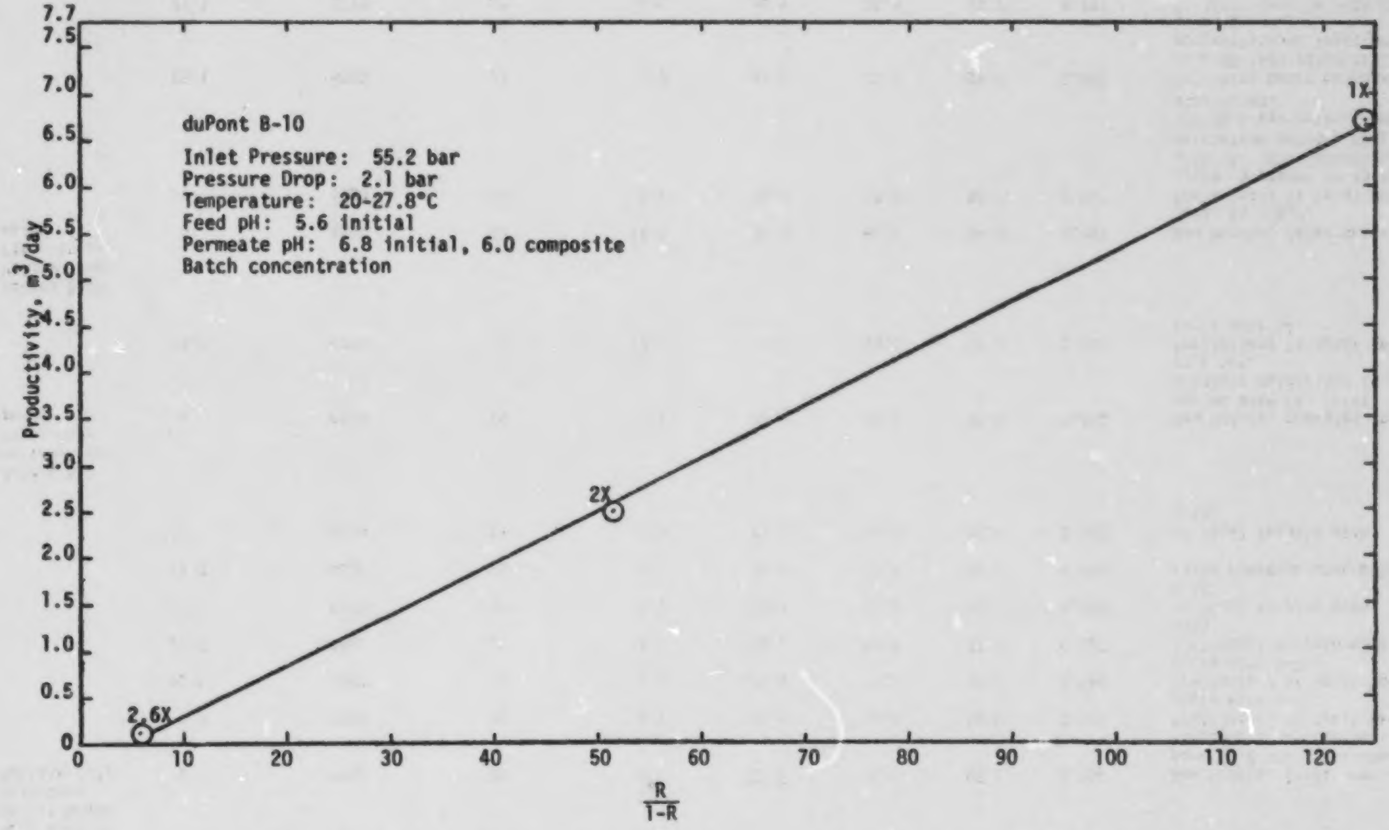

Figure 25. B-10 module productivity as a function of conductivity rejection for the end-of-pipe emulsion crumb ultrafiltrate.

TABLE 26. HISTORY OF SALT REJECTIONS FOR REVERSE OSMOSIS MODULES DURING PROCESSING OF END-OF-PIPE EMULSION CRUMB ULTRAFILTRATE

Module	Cumulative Operating Time (hrs)	Feed Concentration NaCl (ppm)	Temperature (°C)	Permeate Flowrate m³/day	Feed Flowrate m³/day	Conversion %	Rejection %	Intrinsic Rejection	Remarks
Roga 4160 HR Spiral-Wound Cellulose Acetate (CA)	0	3900	26	4.8	28.8	16.7	95.2	0.954	New Module. Inlet pressure 41.2 bar maintained throughout test series.
	9.2	4500	26	4.1	28.9	14.3	94.0	0.943	Preliminary 1X Total Recycle with B-9.
	22.2	4800	25	4.1	28.6	14.7	94.1	0.944	Preliminary 1X Total Recycle with B-10.
	23.0	4550	27	4.5	28.3	16.0	93.3	0.937	2.6X Total Recycle with B-10.
	71.0	5000	27	4.0	28.3	14.2	93.5	0.939	1X Total Recycle with B-10.
	71.3	4900	27	3.9	28.6	13.5	94.1	0.944	1X-2X Pumpdown with B-10.
	102	4450	27	3.8	27.7	13.6	93.6	0.940	2X Total Recycle with B-10.
duPont B-9 Hollow-Fine-Fiber Polyamide	0	4400	26	14.4	24.0	60.2	92.5	0.950	New Module, operated in series with CA. Inlet pressure maintained at 27.6 bar.
	9.2	5200	26	12.2	24.7	49.3	95.9	0.969	Preliminary 1X Total Recycle with CA.
duPont B-10 Hollow-Fine-Fiber Polyamide	0	4500	25	15.5	28.3	54.8	99.6	0.997	New Module. Inlet pressure, 55.2 bar.
	13	5580	25	9.4	24.4	38.5	99.7	0.997	Preliminary 1X Total Recycle. Operated in series with CA. Inlet pressure maintained between 36.6 bar and 38.6 bar unless other wise noted.
	25.1	5360	27	9.9	23.8	41.5	99.6	0.997	Following batch pumpdown to 2.6X feed volumetric concentration. Inlet pressure, 55.2 bar
	73.1	5770	27	8.5	24.3	34.8	99.7	0.997	1X Total Recycle with CA.
	73.4	5630	27	8.1	24.1	32.7	99.7	0.997	1X-2X Pumpdown with CA.
	104	5100	27	6.5	23.9	27.1	99.7	0.997	2X Total Recycle with CA.

TABLE 27. CONTAMINANT ANALYSES FOR REVERSE OSMOSIS (DUPONT B-10) PROCESSING OF END-OF-PIPE EMULSION CRUMB ULTRAFILTRATE

Contaminant	Feed*	Final Concentrate	Initial Permeate	Composite Permeate	Rejection, %†
Total Dissolved Solids (mg/l)	30,480	74,600	166	768	97.5
Suspended Solids (mg/l)	48	113	-	< 5	-
Oil and Grease (mg/l)	5	4	-	< 4	-
TOC (mg/l)	246	578	3	8	96.7
COD (mg/l)	830	1450	8	20	97.6
BOD_5 (mg/l)	12	480	-	1	91.7
Surfactants (mg/l)	0.34	0.75	-	< .05	>85.3
Iron (mg/l)	6.3	7.6	-	< 1	>84.1
Lead (mg/l)	< 1	1.2	-	< 1	-
Color (units)	120	500	-	< 5	>95.8
Turbidity (NTU)	2.4††	2.7	0.25	0.45	>81.3
pH	5.6††	5.4	6.8	6.0	-
Conductivity (μmhos/cm)	30,000	75,000	200	1280	95.7

* Reflects use of spiral-wound ultrafiltration module with pinhole leak

† Rejection, $R = \dfrac{\text{Concentration of Feed - Concentration of Composite Permeate}}{\text{Concentration of Feed}} \times 100$

†† Feed pH adjusted

TABLE 28. COMPARISON OF REVERSE OSMOSIS PERMEATE WITH EFFLUENT GUIDELINES FOR EMULSION CRUMB MANUFACTURING WASTES

Assay	Reverse Osmosis Composite Permeate	BPCTCA	BATEA
COD (mg/ℓ)	20	500	130
BOD_5 (mg/ℓ)	1	25	5
Suspended Solids (mg/ℓ)	< 5	40	10
Oil and Grease (mg/ℓ)	< 4	10	5

The reverse osmosis permeate is seen to satisfy the BPCTCA and BATEA effluent limitation guidelines for all four contaminants. However, under the flux-limiting salt concentrations present in the emulsion crumb ultrafiltrate, treatment by reverse osmosis would be economically prohibitive.

Carbon Adsorption Tests

The equilibrium isotherm at 20°C for the raw emulsion crumb ultrafiltrate is shown in Figure 26. The logarithm of TOC loading (mg TOC adsorbed per gram of carbon) is plotted against the logarithm of the equilibrium TOC concentration. The points fall reasonably close to a straight line indicating agreement with the Freundlich isotherm expression. The initial concentration of the untreated waste, C_0, was 220 mg/ℓ, and the equilibrium loading at this concentration, as determined from the isotherm, was 660 mg TOC/g carbon.

Proposed effluent guidelines for BATEA treatment of emulsion crumb wastes require an effluent COD of approximately 130 mg/ℓ. The measured ratio of COD to TOC for the raw emulsion crumb ultrafiltrate was 3.4.* Therefore, the equivalent TOC concentration to meet the proposed BATEA guideline is 38 mg/ℓ.

If a sharp breakthrough curve could be obtained for processing of this waste through a carbon column, the carbon would have a TOC loading of 660 mg/g carbon at breakthrough. To decrease the TOC of the waste from 220 mg/ℓ to 38 mg/ℓ would require a carbon dosage of 0.28 kg/m^3 (2300 lbs/MM gal). Extrapolation of cost data for municipal waste treatment (10) indicates a treatment cost of about \$0.12/m^3 (\$0.45/1000 gal) for a typical plant (4) producing 5,678 m^3 (1.5 MM gal) of waste per day. This cost is relatively low for the treatment of industrial wastes.

However, it is very unlikely that a sharp breakthrough curve would be obtained for the treatment of this waste. This is indicated by the steep slope of the isotherm. As the TOC concentration decreases, the loading drops off very rapidly. For a twofold decrease in concentration (from 220 to 110 mg/ℓ), the adsorptive capacity of the carbon decreases by more than an

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* Historical COD to TOC ratios, from plant records, averages 2.8 to 2.9.

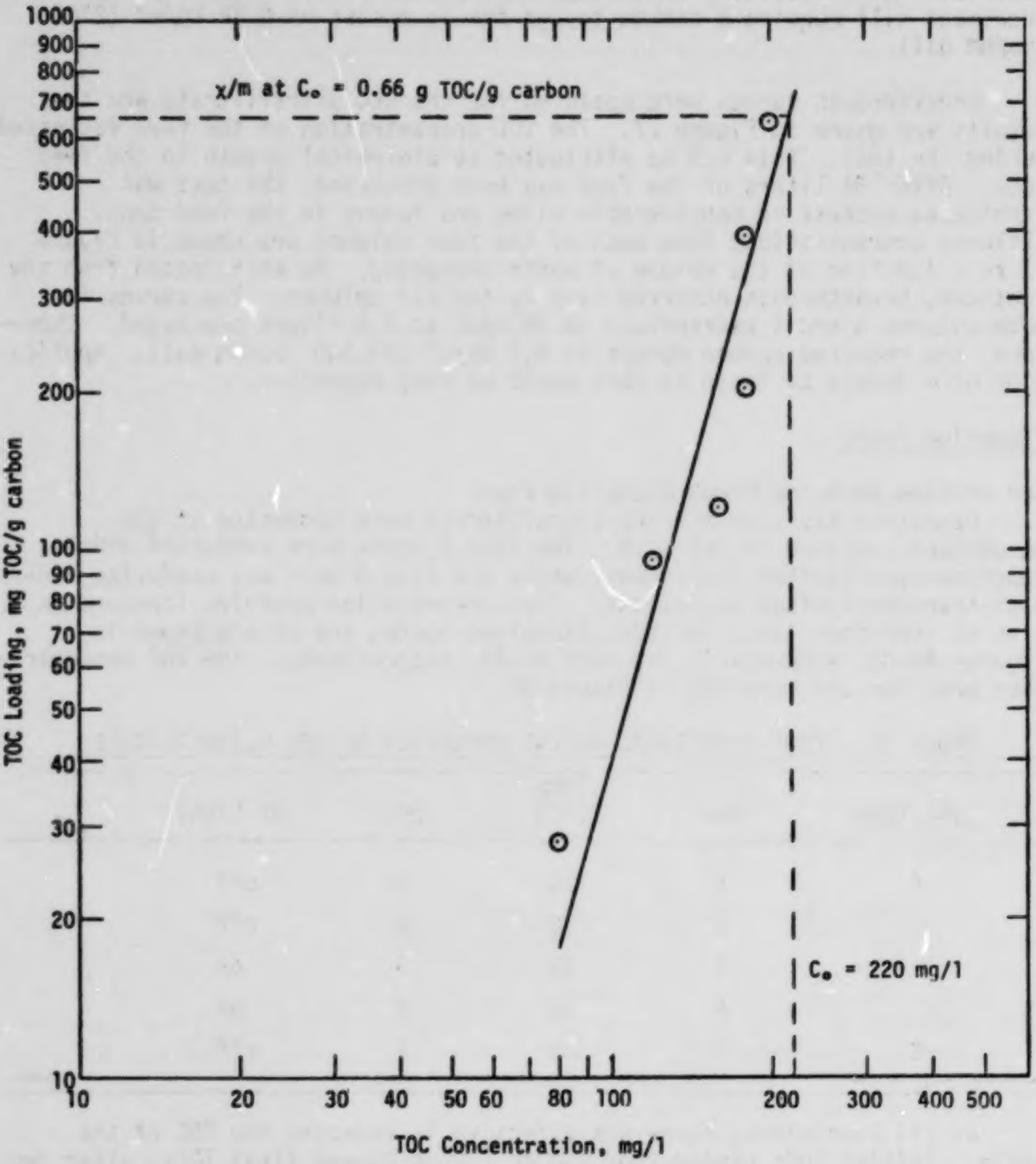

Figure 26. Equilibrium adsorption isotherm at 20°C for end of pipe emulsion crumb ultrafiltration.

order of magnitude. This indicates that the waste is composed of a small amount of strongly adsorbed material and a larger amount of weakly adsorbed material. As a result, breakthrough will probably occur very rapidly and treatment will require a carbon dosage far in excess of 0.28 kg/m³ (2300 lbs/MM gal).

Breakthrough curves were measured for the REC ultrafiltrate and the results are given in Figure 27. The TOC concentration of the feed decreased during the test. This can be attributed to biological growth in the feed tank. After 64 liters of the feed had been processed, the test was terminated because of considerable slime and fungus in the feed tank. Effluent concentrations from each of the four columns are shown in Figure 27 as a function of the volume of waste processed. As anticipated from the isotherm, breakthrough occurred rapidly for all columns. The curves for both columns 3 and 4 extrapolate to 38 mg/ℓ at 7.5 liters processed. Therefore, the required carbon dosage is 5.2 kg/m³ (43,300 lbs/MM gal). Application of a dosage as large as this would be very expensive.

Ozonation Tests

End-of-Pipe Emulsion Crumb Ultrafiltrate--

Ozonation tests on the REC ultrafiltrate were conducted at the conditions outlined in Table 29. The Type A tests were conducted under reaction-rate-limited conditions, while the Type B test was conducted under mass-transfer-limited conditions. The concentration profiles (concentration vs. reaction time) for TOC, dissolved ozone, and pH are shown in Figures A3-A6, Appendix A, for runs A1-A4, respectively. The TOC concentration profiles are compared in Figure 28.

TABLE 29. TEST CONDITIONS DURING OZONATION OF REC ULTRAFILTRATE

Test Type	Run	Temp (°C)	pH	UV Light
A	1	30	5	off
	2	30	9	off
	3	30	5	on
	4	30	9	on
B	1	30	9	off

At all conditions, ozone was effective in reducing the TOC of the waste. Initial TOCs ranged from 200 to 220 mg/ℓ, and final TOCs, after two hours of reaction time, ranged from 10 to 30 mg/ℓ. At pH 5, there was no significant effect of UV light on the rate of reaction. A good straight-line semi-logarithmic correlation is obtained indicating that the reaction is pseudo-first-order with respect to TOC. That is, the rate equation

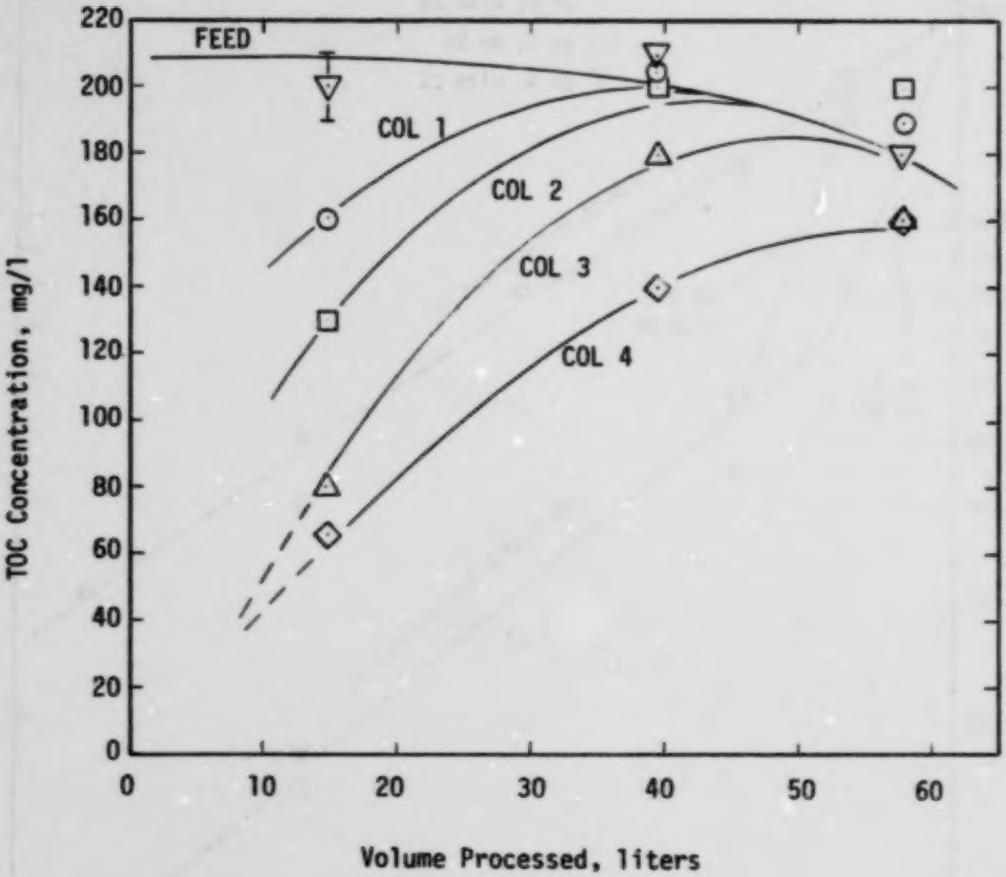

Figure 27. TOC breakthrough curves for carbon column treatment of end-of-pipe emulsion crumb ultrafiltrate.

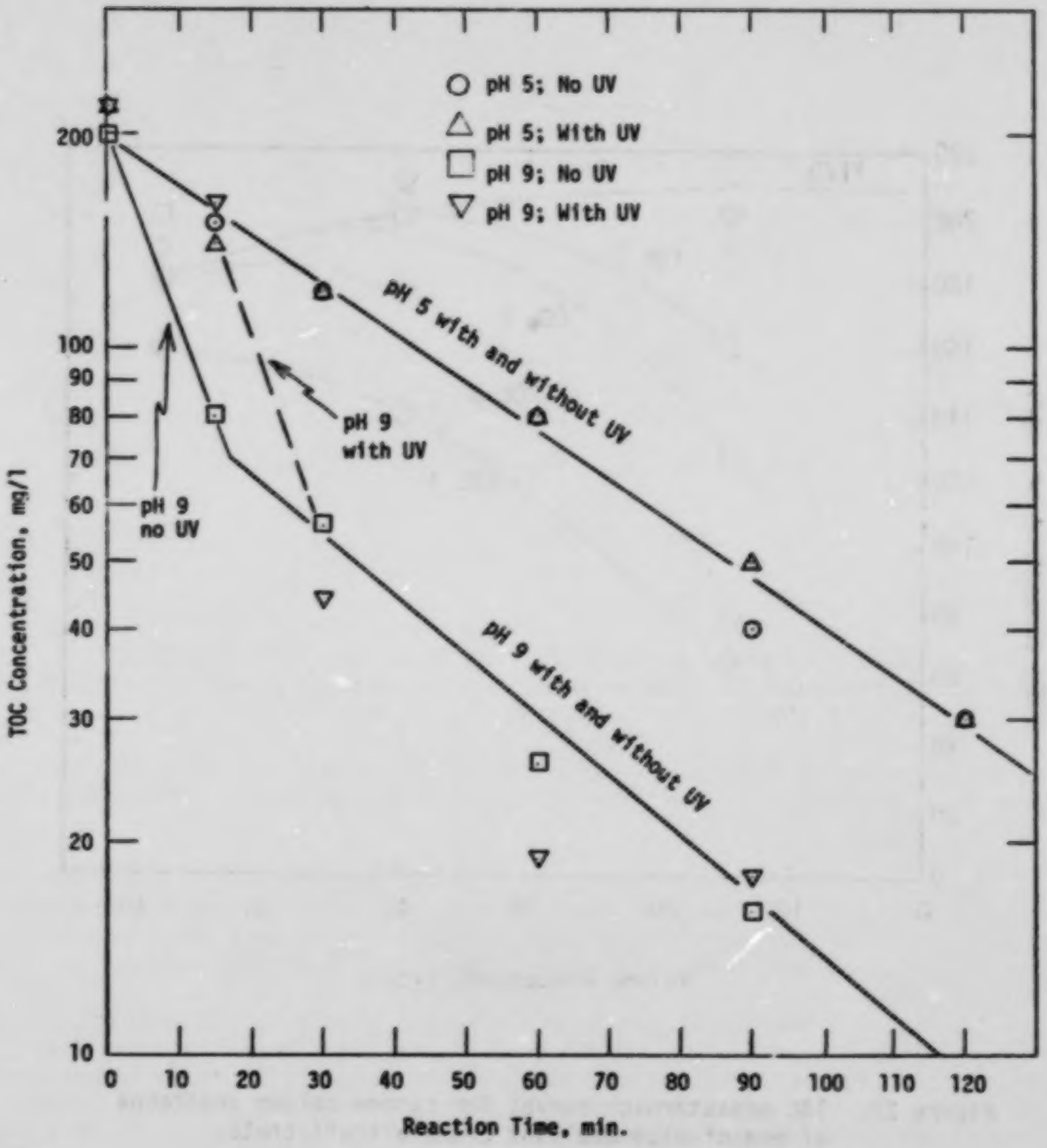

Figure 28. TOC vs. reaction time at various conditions for ozonation of end of pipe emulsion crumb ultrafiltrate.

is given by:

$$\frac{-dC}{dt} = kC \qquad (1)$$

where

C = TOC concentration
t = Reaction time
k = Rate constant

Integration gives:

$$\log \frac{C}{C_0} = \frac{kt}{2.303} \qquad (2)$$

where

C_0 = Initial TOC concentration

Thus, the slope of the plot of log C vs. t is proportional to the first-order rate constant, k.

At pH 9 without UV light, the TOC dropped rapidly over the first 15 to 20 minutes. During this time period the dissolved ozone concentration remained close to zero indicating that mass transfer was rate limiting during this period and that the rate of reaction was very fast. Thus, the use of alkaline conditions dramatically increases the initial rate of reaction. After about 20 minutes, reaction occurred at a much slower rate, but at a somewhat higher rate than at pH 5.

It can also be observed from Figure 28 that after 30 minutes of reaction there is no significant difference in reaction rate with and without UV light.

The results of a Type B test at 30°C, pH 9, and without UV light are shown in Figure 29. Because of the high initial TOC of this waste, the test procedure was modified somewhat. During the first half hour of ozonation, Type A test conditions were used (1.42 m^3/hr @ STP, 2 wt % O_3 in feed).

Over the 3.5 hours of reaction under Type B conditions, the TOC decreased from 108 to 59 mg/ℓ (circles of Figure 29). From the known flow rate of ozone to the contactor and the measured decrease in ozone concentration across the contactor, it is possible to calculate the amount of ozone consumed per liter of waste. Based on the assumptions that there is only one active oxygen atom per molecule of ozone, that ozone provides the only source of oxygen, and that the oxygen demand of the contaminants is associated entirely with the organic carbon, the theoretical ratio of ozone consumed

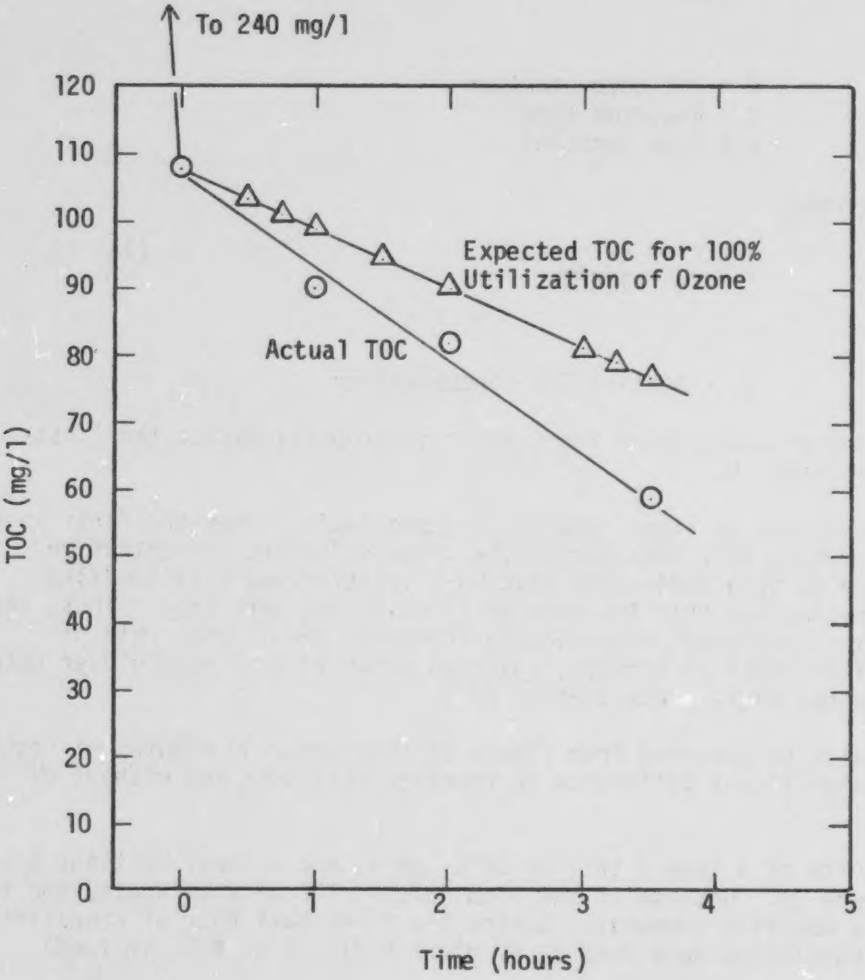

Figure 29. Ozonation of end-of-pipe emulsion crumb ultrafiltrate at 30°C and pH 9 without UV light (type B).

to TOC oxidized is:

$$\frac{32\ \text{mg O}}{12\ \text{mg TOC}} \times \frac{48\ \text{mg O}_3}{16\ \text{mg O}} = 8\ \frac{\text{mg O}_3}{\text{mg TOC}} \qquad (3)$$

With this ratio and the measured ozone consumption, one can calculate a theoretical or expected TOC decline (triangles of Figure 29) for 100% utilization of ozone for organics oxidation.

The ozone utilization efficiency for reaction with organics is defined as:

$$\frac{(\Delta\text{TOC})_a}{(\Delta\text{TOC})_c} \times 100\% \qquad (4)$$

where

$(\Delta\text{TOC})_a$ = actual TOC decrease for a given reaction time
$(\Delta\text{TOC})_c$ = calculated TOC decrease for the same reaction time

As shown in Figure 29, the TOC decreased more rapidly than expected based on 100% utilization of the ozone. There are several possible explanations. First, it is possible that more than a single atom of oxygen per ozone molecule participates in the oxidation reaction. This oxygen could come from the ozone molecule, from dissolved molecular oxygen, or from organic oxygen in the contaminants (e.g., acids, ketones, etc.). It is also possible that reaction under Type A conditions during the first half-hour produced many partial oxidation products. These products would require less ozone to complete the oxidation than expected on the basis of the above assumptions and calculations. Unfortunately, there was insufficient waste remaining to check this latter hypothesis.

The ozone utilization efficiency from Figure 29 is 158%. This indicates an ozone consumption of 5 mg O_3 per mg TOC rather than the assumed value of 8. Thus, ozone appears to be very efficient for the ozonation of raw emulsion crumb ultrafiltrate. Unfortunately, the TOC level of the ultrafiltrate is relatively high, which adversely affects the economics for ozonation of this waste.

End-of-Pipe Emulsion Crumb Reverse Osmosis Permeate--
The objective of these tests was to determine the effect of temperature, pH, and UV light on the rate of organics removal should polishing of the reverse osmosis permeate become necessary. Eight tests were conducted with REC reverse osmosis permeate. The test conditions and results are given in Table 30. Because of the low levels of TOC in the samples, there is a rather large uncertainty in the analyses. For many of the runs, the TOC did not decrease continuously with reaction time as would be expected.

TABLE 30. TEST CONDITIONS AND RESULTS FOR OZONATION OF END-OF-PIPE EMULSION CRUMB REVERSE OSMOSIS PERMEATE

Run	Temperature (°C)	pH	UV Light	Reaction Time (min)	Dissolved O_3 (mg/1)	TOC (mg/1)	Time to 50% Conversion (min)
1	30	5	off	0	-	6	90
				15	-	3	
				30	-	6	
				60	4.3	4	
				90	8.1	3	
				120	7.0	-	
2	30	9	off	0	3.7	6	60
				15	1.4	4	
				30	3.4	6	
				60	2.5	3	
				90	2.4	3	
				120	-	-	
3	30	5	on	0	4.9	8	>120
				15	6.0	5	
				30	9.5	6	
				60	7.2	6	
				90	6.5	7	
				120	7.2	6	
4	30	9	on	0	-	8	>120
				15	0.4	8	
				30	0.3	4	
				60	< 0.2	5	
				90	< 0.2	6	
				120	< 0.2	6	

(Continued)

TABLE 30. (Continued)

Run	Temperature (°C)	pH	UV Light	Reaction Time (min)	Dissolved O_3 (mg/l)	TOC (mg/l)	Time to 50% Conversion (min)
5	45	5	on	0	2.0	6	30
				15	4.4	4	
				30	3.9	3	
				60	4.8	3	
				90	5.0	1	
				120	8.0	1	
6	45	9	on	0	1.2	6	15
				15	0.85	2	
				30	0.76	1	
				60	< 0.2	0	
				90	< 0.2	1	
				120	< 0.2	3	
7	45	5	off	0	2.6	7	60
				15	3.3	7	
				30	3.5	5	
				60	4.5	3	
				90	5.5	4	
				120	7.5	5	
8	45	9	off	0	0.55	7	15
				15	1.0	3	
				30	1.0	2	
				60	1.1	3	
				90	0.55	2	
				120	0.60	2	

Judging from the magnitude of the deviations from a continuous TOC decrease, the analytical error may be as high as ± 2 mg/ℓ for some samples. [The specified accuracy of the instrument used (Dohrmann DC-50) is ± 1 mg/ℓ in this range.] Since the relative error for these analyses is substantial, conclusions can be drawn only with some uncertainty. Nevertheless, the final column of Table 30 gives the estimated time required for 50% conversion of TOC to CO_2.

Based on these times, the following conclusions are tentatively drawn for ozonation of raw emulsion crumb reverse osmosis permeate.

- Without UV light at 30°C, there is probably no significant difference in the reaction rates at pH 5 and pH 9.
- Increasing the temperature from 30°C to 45°C (without UV light) has no significant effect on the reaction rate at pH 5, but significantly increases the reaction rate at pH 9.
- The use of UV light at 30°C appears to inhibit the reaction both at pH 5 and pH 9, but at 45°C UV light does not inhibit the reaction and may promote the reaction rate slightly, particularly at pH 5.
- The most rapid rate of reaction occurs at 45°C and pH 9. At these conditions, UV light has no significant effect.

End-of-Pipe Emulsion Crumb Carbon Column Effluent--

Both Type A and Type B ozonation tests were conducted with the REC waste after ultrafiltration and activated carbon treatment. The TOC of the composite effluent from the carbon columns was ~100 mg/ℓ.

Table 31 presents the experimental conditions for the Type A tests. The TOC vs. Time curves for tests A-1 through A-4 are compared in Figure 30. The data on which Figure 30 is based are given in Appendix A. The results shown in Figure 30 are quite similar to those presented for ozonation of raw emulsion crumb ultrafiltrate (see Figure 28). The rate of reaction at low pH is very slow. Irradiation with UV light appears to increase the rate of reaction somewhat, but still the rate of reaction is probably too slow for economical application of ozone at these conditions. On the other hand, the rate of reaction at high pH is reasonably rapid. Again, UV irradiation increases the rate slightly, but not enough to justify the use of UV in a practical system.

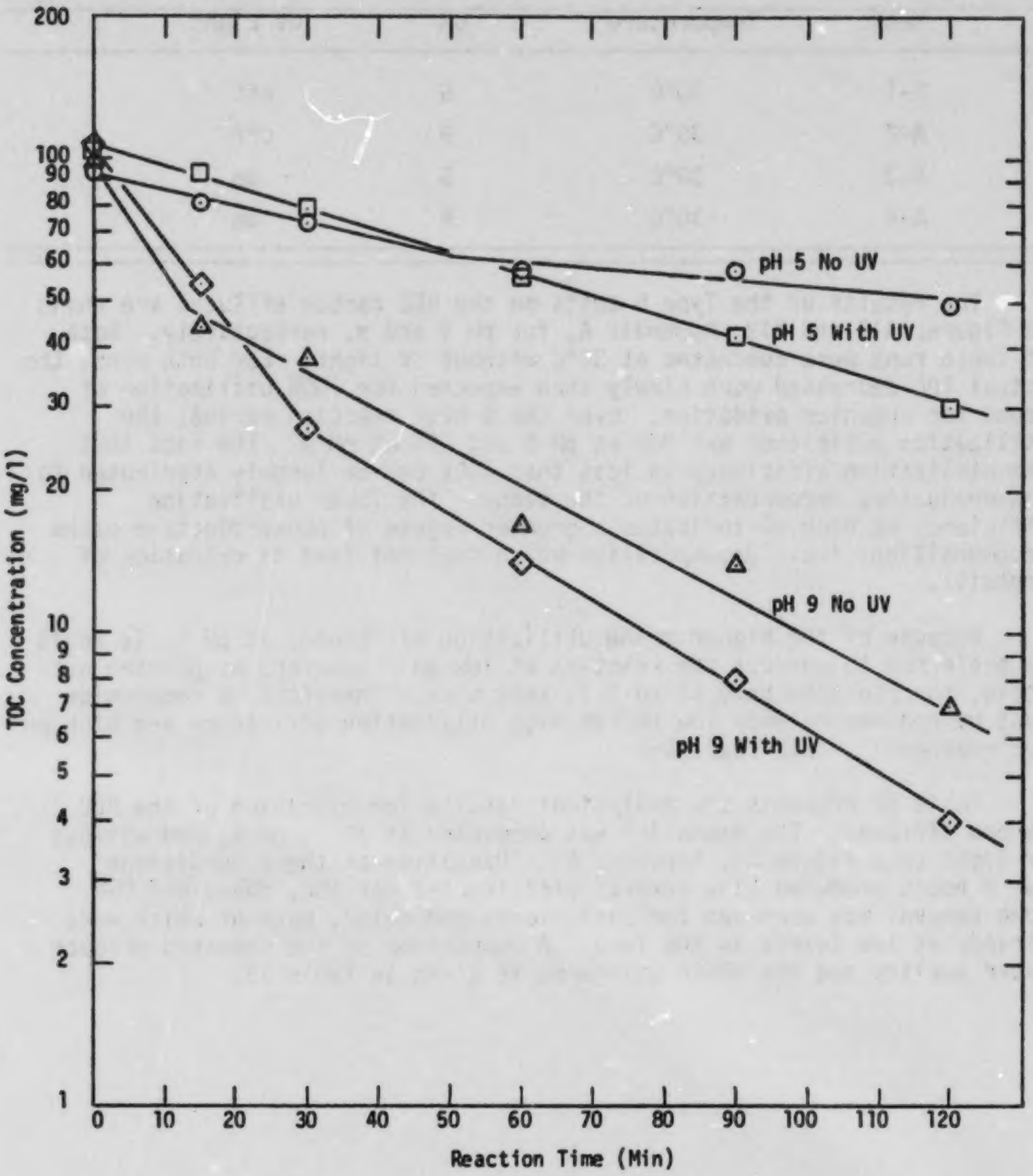

Figure 30. Comparison of TOC vs. time curves for ozonation of end-of-pipe emulsion crumb carbon effluent at various conditions.

TABLE 31. TEST CONDITIONS DURING OZONATION OF REC CARBON COLUMN EFFLUENT

Test	Temperature	pH	UV Light
A-1	30°C	5	off
A-2	30°C	9	off
A-3	30°C	5	on
A-4	30°C	9	on

The results of the Type B tests on the REC carbon effluent are shown in Figures A11 and A12, Appendix A, for pH 5 and 9, respectively. Both of these runs were conducted at 30°C without UV light. For both runs, the actual TOC decreased more slowly than expected for 100% utilization of ozone for organics oxidation. Over the 6 hour reaction period, the utilization efficiency was 80% at pH 5 and 62% at pH 9. The fact that the utilization efficiency is less than 100% can be largely attributed to non-productive decomposition of the ozone. The lower utilization efficiency at high pH indicates a greater degree of non-productive ozone decomposition; i.e., decomposition which does not lead to oxidation of organics.

Because of the higher ozone utilization efficiency at pH 5, it would be preferred to conduct the reaction at low pH. However, as pointed out above, the reaction rate at pH 5 is very slow. Therefore, a compromise must be reached between low pH for high utilization efficiency and high pH for reasonably rapid reaction.

Table 32 presents the analytical results for ozonation of the REC carbon effluent. The ozonation was conducted at 30°C, pH 9, and without UV light (see Figure A8, Appendix A). Ozonation at these conditions for 2 hours produced high removal efficiencies for TOC, BOD_5, and COD. Some removal was achieved for surfactants and color, both of which were already at low levels in the feed. A comparison of the ozonated product water quality and the BATEA standards is given in Table 33.

TABLE 32. CONTAMINANT ANALYSES FOR OZONATION OF END-OF-PIPE EMULSION CRUMB CARBON EFFLUENT

Assay	Concentration Before Ozonation[*] (mg/l)	Concentration After Ozonation[*] (mg/l)	Removal Efficiency (%)
TDS	29,600	28,600	3
SS	40[†]	60	< 0
Oil and Grease	< 4.0	5.4	< 0
Surfactant	0.51	0.39	23
Fe	5.2	5.1	0
Pb	< 1.0	< 1.0	-
Color	50 units	40	20
TOC	100	10	90
BOD_5	20	3	85
COD	438	44[††]	90

[*] Ozonated for 2 hours at 30°C, pH 9, without UV light. Concentration profiles shown in Figure A8 .

[†] The high reading is due to a pinhole leak in the spiral-wound ultrafiltration module.

[††] Original assay was in error and insufficient sample remained to repeat assay, therefore, value given is based on the carbon effluent COD/TOC ratio of 4.38.

TABLE 33. COMPARISON OF OZONATED REC CARBON EFFLUENT PRODUCT WATER WITH EFFLUENT GUIDELINES FOR EMULSION CRUMB MANUFACTURING WASTES

Assay	REC Carbon Effluent Ozonated Product Water	BATEA
COD (mg/ℓ)	44*	130
BOD_5 (mg/ℓ)	3	5
Suspended Solids (mg/ℓ)	60	10
Oil and Grease (mg/ℓ)	5.4	5

*Based on carbon effluent COD/TOC ratio of 4.38.

Only the suspended solids content in the ozonated effluent appreciably exceeds the BATEA standard. These solids are principally the result of a pinhole leak in the spiral wound module used during the ultrafiltration tests. Under actual field conditions, a suspended solids content of <4 mg/ℓ is to be expected.

EXPERIMENTAL RESULTS FOR SECONDARY TREATED EMULSION CRUMB WASTEWATER

Proposed BATEA Treatment

Dual-Media Depth Filtration--

Filter Performance--Filtrate turbidity and column headloss are plotted as functions of operating time in Figure 31 for the processing of the secondary emulsion crumb (SEC) effluent through the 0.05 m diameter dual-media depth filter. The feed turbidity was 17 NTU, as received, and 10 NTU following pH adjustment to pH = 7.1 with 1N NaOH solution. As observed in Figure 31, the filtrate turbidity throughout the first 20 hours of column operation remained below 3 NTU, and except for the start-up period, was below 2.5 NTU. This represents a turbidity reduction of greater than 75%. During the 21st hour, a substantial turbidity increase to 5.7 NTU occurred, after which filtrate quality improved slightly. When filtrate turbidity exceeded 6 NTU, the run was terminated. This occurred after 0.32 m^3 (84 gal) had been processed through the column and 34 operating hours had elapsed.

At no point during the run did the column headloss exceed 0.21 bar (3 psig), indicating that substantial surface straining did not occur. In terms of both turbidity reduction and filter run length, the performance of the anthracite/silica sand filter on SEC effluent was acceptable.

The filtrate turbidity versus time plot for the processing of the SEC wastewater with the 0.23 m diameter column is presented in Figure A13, Appendix A. Following an initial unsteady period, the filtrate turbidity remained

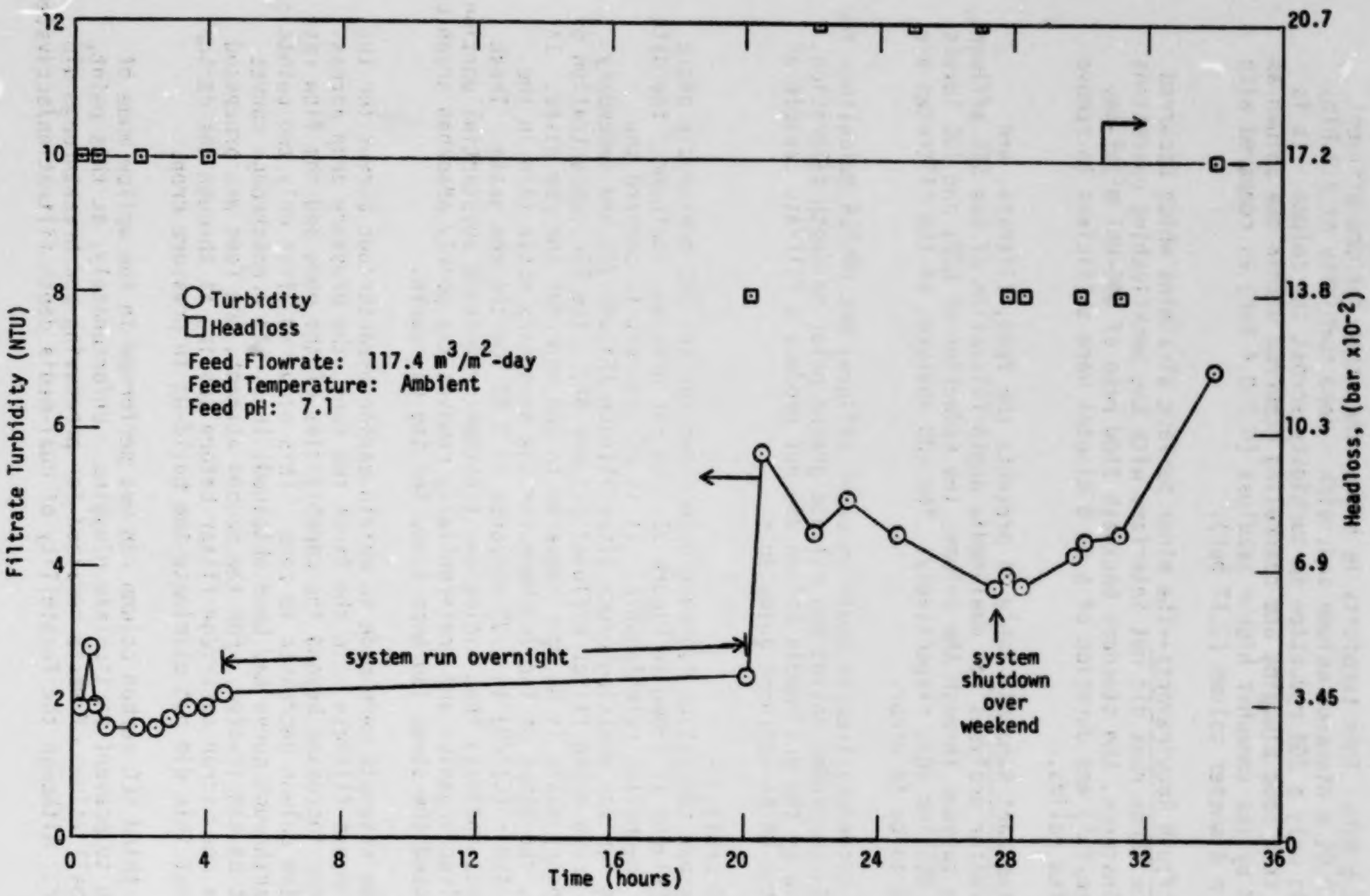

Figure 31. Filtrate turbidity and column headloss vs. time for dual-media depth filtration of secondary treated emulsion crumb wastewater; 0.05 m diameter column.

stable at 5 NTU. This turbidity is higher than that for the effluent from the 0.05 m diameter column and, with a feed turbidity of 7.2 NTU, represents only a 30% reduction in turbidity across the column. It is possible that some plugging and channeling occurred within the column as indicated by the somewhat higher headloss (0.2-0.4 bar) as compared with the 0.05 m diameter column (0.17 bar).

Backflush Requirements--The minor surface straining which occurred during the three runs did not interfere with the backflushing operations. In each instance, the standard backwash flow rate of 646-881 m^3/m^2-day (11-15 gpm/ft^2) and duration of 6 to 8 minutes were sufficient to remove accumulated solids.

Contaminant Removal--Table 34 presents the feed, filtrate, and backwash-water analyses for dual-media depth filtration of the SEC effluent. Following passage through the column, the reduction of BOD_5 and TOC levels averaged 66% and 10%, respectively. The COD analyses of the filtrates are suspected to be in error.

The secondary treated emulsion crumb effluent met BPCTCA guidelines for BOD_5, COD, suspended solids and oil and grease prior to depth filtration. Processing by the dual-media column did not produce a filtrate capable of meeting the BATEA effluent guidelines.

Carbon Adsorption--

A carbon adsorption isotherm determined for the SEC dual-media depth filter effluent is shown in Figure 32. As for previous isotherms, the data follow a Freundlich relationship. It is of interest to compare the isotherms for raw emulsion crumb ultrafiltrate (Figure 26) and secondary emulsion crumb depth filter effluent (Figure 32). The TOC concentration of the secondary waste is 58 mg/ℓ compared to 220 mg/ℓ for the raw waste. In addition, the slope of the isotherm for the secondary waste (1/n in the equation $X/m = (C)^{1/n}$) is 1.32 compared to 3.57 for the raw waste. These differences indicate that biological treatment removes a substantial portion of dissolved organics and preferentially removes the poorly adsorbed organics which caused the steep isotherm slope for the raw waste.

Three attempts were made to obtain carbon breakthrough curves for the SEC dual-media filtrate. In the first two runs, the pressure drop across the columns increased beyond the capabilities of the pump and the flow rate through the column decreased to zero. This occurred after only two points on each breakthrough curve had been obtained; thus, the breakthrough curves could not be constructed. For the second attempt, the feed was processed through a one-micron cartridge filter before passing it through the carbon column, but this did not eliminate the build-up in pressure drop.

The third SEC carbon column run was performed in the upflow mode of operation to prevent particulate plugging. Unfortunately, at this point, only a small volume of waste remained for processing and breakthrough did not occur. Although the feasibility of dual-media depth filtration/activated

TABLE 34. CONTAMINANT ANALYSES FOR DUAL-MEDIA DEPTH FILTRATION OF SECONDARY TREATED EMULSION CRUMB WASTEWATER

Contaminant	Raw Feed	pH Adjusted Feed	0.05m Diameter Column Backwash	0.23m Diameter Column Composite Filtrate	0.05m Diameter Column Composite Filtrate
Total Dissolved Solids (mg/l)	13,870	14,650	15,300	14,240	14,330
Suspended Solids (mg/l)	37	39	203	27	27
Oil and Grease (mg/l)	-	< 4	12	8	4.7
TOC (mg/l)	72	72	100	66	64
COD (mg/l)	372	206	438	(511)	(468)
BOD_5 (mg/l)	< 1	40	10	16	10
Surfactants (mg/l)	-	1.0	4.2	1.3	7.2
Iron (mg/l)	-	3.2	7.8	2.7	1.9
Lead (mg/l)	-	0.6	< 1.0	0.5	< 0.5
Color (units)	200	225	300	200	200
Turbidity (NTU)	17	10	~30	5.4	4.2
pH	2.3	7.1	7.0	7.0	6.8
Conductivity (µmhos/cm)	19,000	17,000	16,500	17,000	16,000

Note: ( ) indicates suspected error in analyses

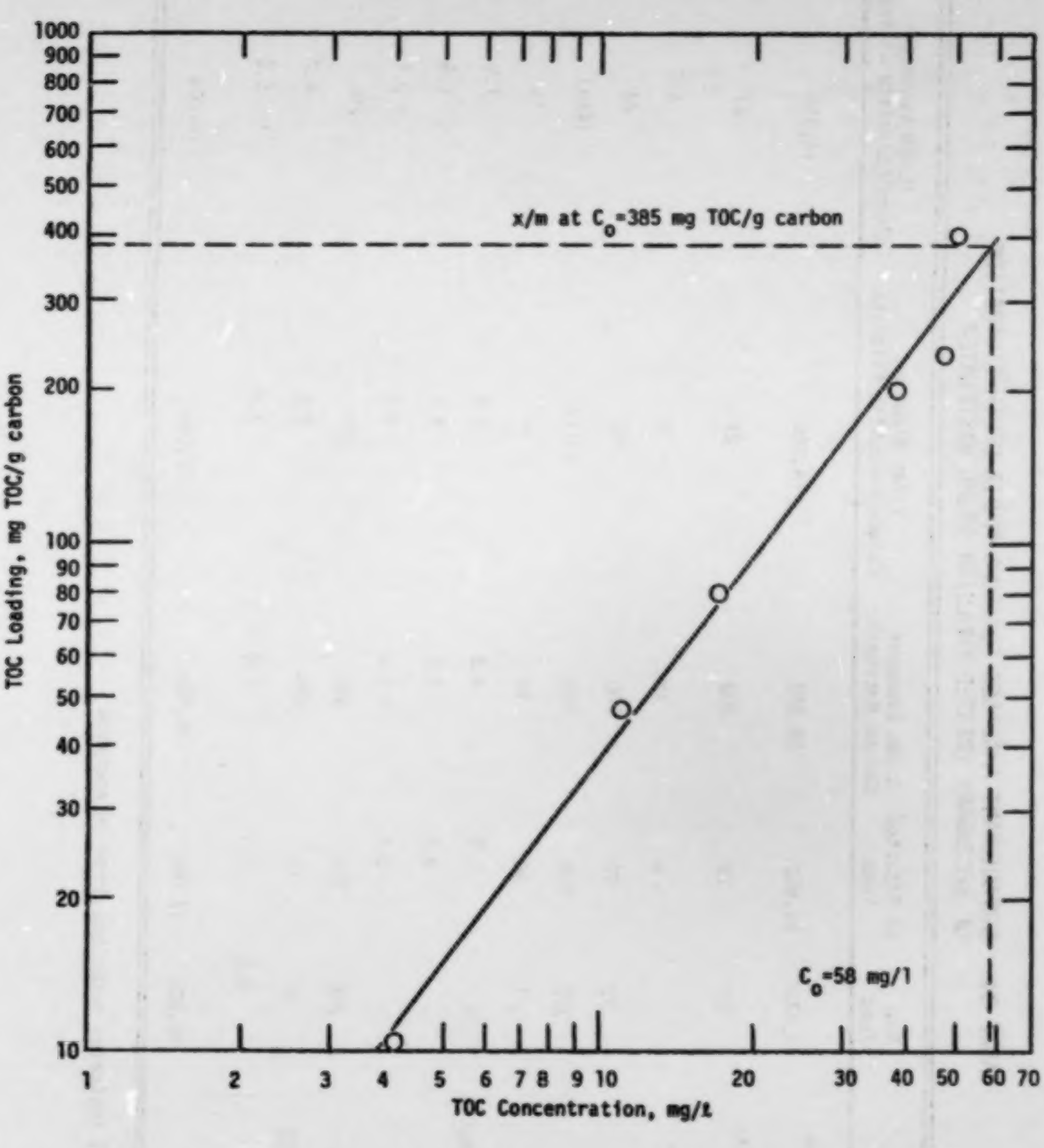

Figure 32. Equilibrium adsorption isotherm at 20°C for secondary treated emulsion crumb depth filter effluent.

carbon treatment of SEC wastewaters was demonstrated, further testing is necessary to develop an accurate economic profile of the process.

Reverse Osmosis Tests

Selection of Preferred Membrane--

The duPont B-10 polyamide module was chosen for the initial batch processing of the depth filter effluent because of the high dissolved solids loading of the SEC wastewater. The B-10 module has the highest operating pressure of the reverse osmosis modules studied during this program and is, therefore, best suited to handle the high osmotic pressure exerted by the dissolved salts in the feed. During a second batch concentration (see below) and the total recycle tests, the ROGA CA module was added in series ahead of the B-10. The narrow-channel, spiral-wound CA module is less susceptible to plugging than the hollow-fine-fiber B-10 permeator and may be preferred if future modules are developed with higher pressure ratings.

Module Productivity--

The B-10 permeate flow rate as a function of conductivity rejection during a batch pumpdown of the SEC dual-media depth filter effluent is shown in Figure 33. The productivity of the B-10 module decreased from 6.6 m^3/day (1.2 gpm) initially to 0.72 m^3/day (0.13 gpm) at a 4.2X volumetric feed concentration. Concentration beyond this point was judged to be uneconomical for full-scale operation.

The non-linearity of the flux/rejection relationship implies that osmotic pressure was not the only factor limiting module productivity. Module fouling during the latter stages of the batch concentration appears to have reduced permeator output.

A second reverse osmosis batch concentration was performed with the spiral-wound CA module operated in series with the B-10 module. The test system was operated at the maximum pressure (41.4 bars [600 psig]) recommended for the CA module. The permeator productivities for this experiment are presented in Figure 34 as a function of the conductivity rejection. The spiral-wound module can be seen to be less susceptible to fouling than the hollow-fiber module since its flux/rejection curve follows the expected linear relationship. The permeate flow rates for the B-10 module during this test are lower since the module was operating at an inlet pressure of 36.6-37.9 bar (530-550 psig). The characteristics of the curves developed for the B-10 module (shown in Figures 33 and 34) are, however, quite similar.

The CA and B-10 modules were exposed to the SEC dual-media depth filter effluent for extended time periods during total recycle experiments at 1X, 2X, and 4X volumetric feed concentrations. The permeate flow rates during these experiments are presented in Figure 35 as a function of operating time. At all three concentrations, the productivity of the spiral-

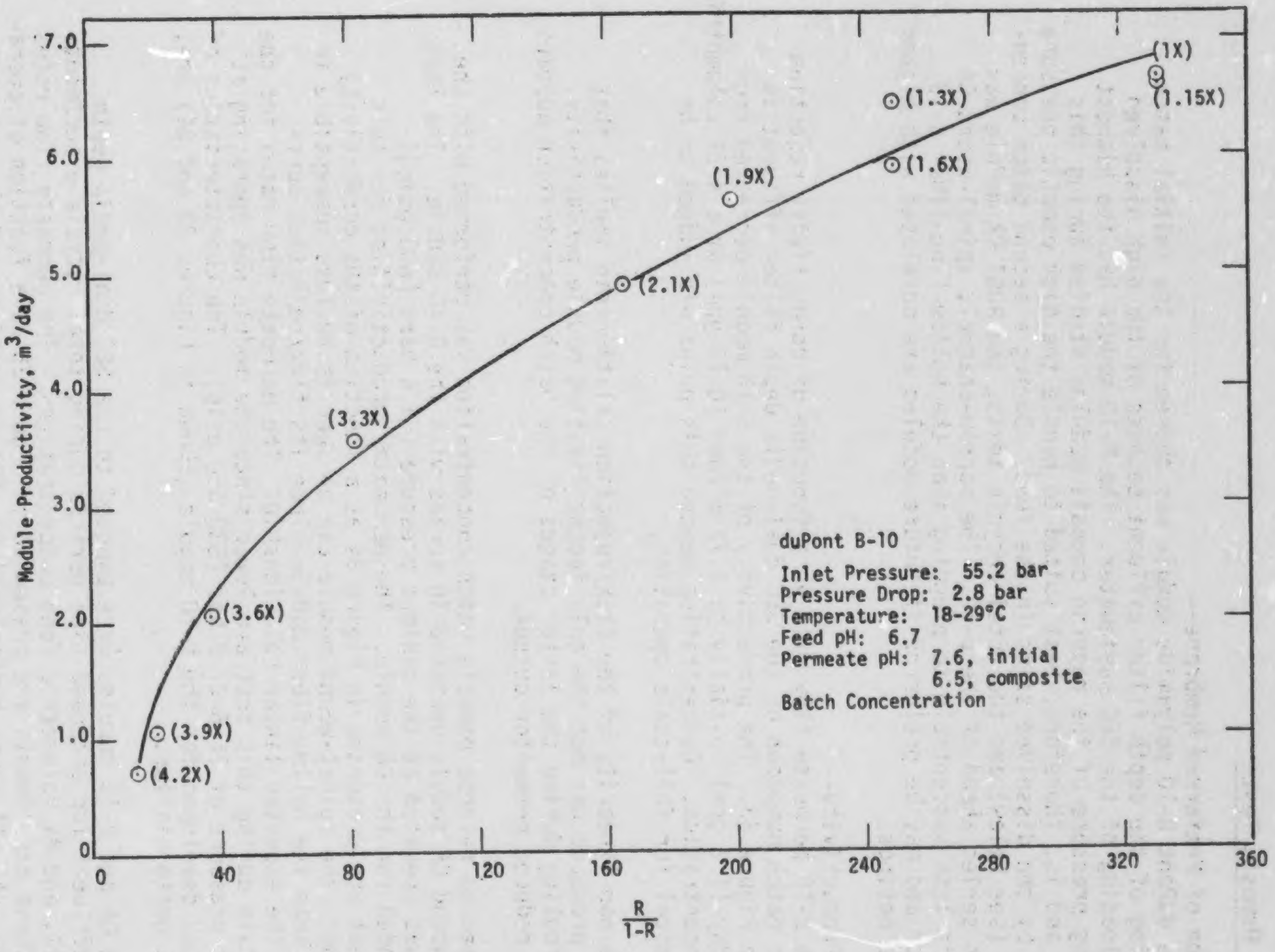

Figure 33. B-10 module productivity as a function of conductivity rejection for secondary treated emulsion crumb dual-media filtrate, first processing period.

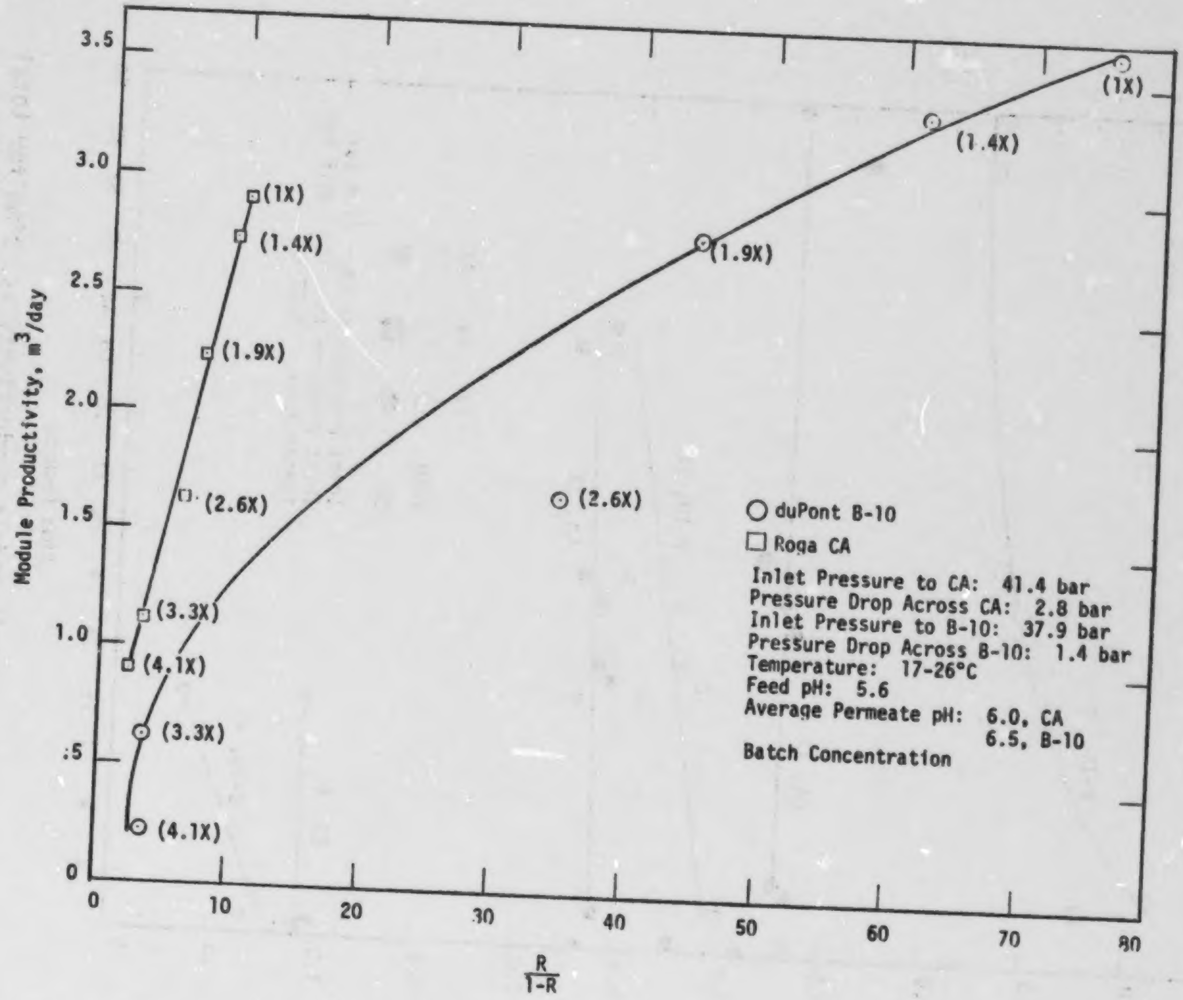

Figure 34. Reverse osmosis module productivity as a function of conductivity rejection for secondary treated emulsion crumb dual media filtrate, second processing period.

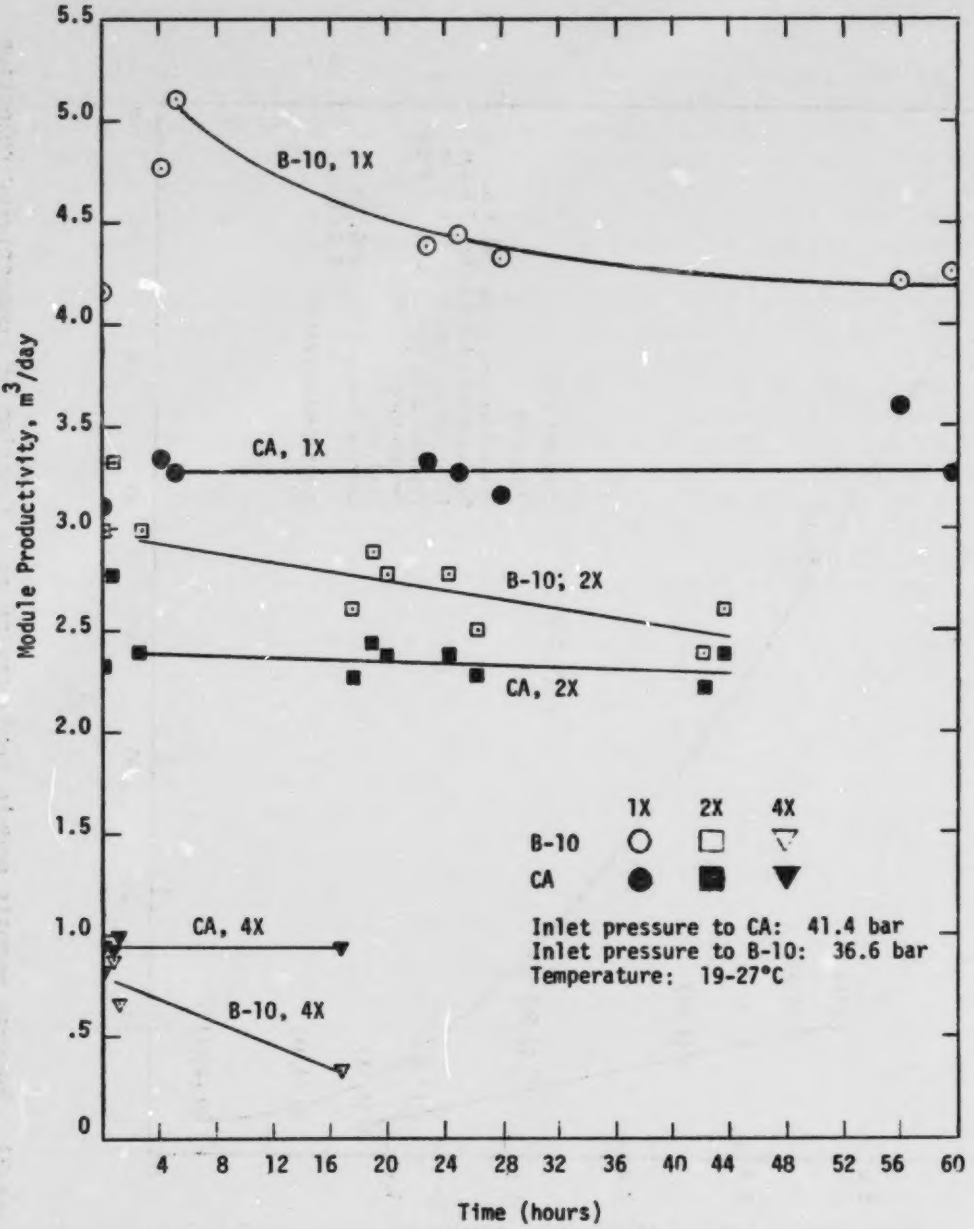

Figure 35. Reverse osmosis module productivity vs. time for total recycle life tests with secondary treated emulsion crumb dual-media filtrate.

wound module remained relatively stable while the productivity of the hollow-fiber B-10 permeator declined with time. This is further indication that some fouling of the hollow-fiber membranes was occurring.

The performance history of the reverse osmosis modules during processing of the SEC depth filter effluent is indicated by the standard NaCl test results given in Table A3, Appendix A. A 23% flux decline was observed for the CA module during 124 hours of exposure to this waste stream, while the B-10 module exhibited a 65% flux decline for the same exposure. The overall NaCl rejections for both modules decreased slightly, even though periodic increases in rejection were noted.

It is suspected that the suspended solids of the reverse osmosis feed were not sufficiently reduced by the 5 μ and 1 μ string-wound cartridge filters used for pretreatment. This probably resulted in fouling of the B-10 module and, to a lesser degree, the CA module. Standard cleaning procedures for removal of colloidal matter from the permeators were employed and were successful in restoring the productivity and NaCl rejection of both modules to pre-exposure levels. No irreversible membrane fouling or degradation due to environmental attack was noted.

Module Rejection--

Feed, composite permeate, and final concentrate analyses for the batch concentration of SEC dual-media depth filter effluent to a volumetric concentration of 4.2X are presented in Table 35. Contaminant rejections are also shown. The B-10 module exhibited rejections of 64%, 99%, and 88% for BOD_5, COD, and TOC, respectively. The analyses which are common to the development document guidelines are compared in Table 36. The contaminant levels in the reverse osmosis permeate are lower than required to meet the BATEA effluent limitation guidelines for all four pollutant parameters, and the extent of COD removal is exceptionally impressive.

TABLE 36. COMPARISON OF SEC REVERSE OSMOSIS PERMEATE WITH EFFLUENT GUIDELINES FOR EMULSION CRUMB MANUFACTURING WASTES

Assay	Reverse Osmosis Composite Permeate	BATEA
COD (mg/ℓ)	6	130
BOD_5 (mg/ℓ)	4	5
Suspended Solids (mg/ℓ)	<4	10
Oil and Grease (mg/ℓ)	<4	5

TABLE 35. CONTAMINANT ANALYSES FOR REVERSE OSMOSIS (DUPONT B-10) PROCESSING OF SECONDARY TREATED EMULSION CRUMB DEPTH FILTER EFFLUENT

Contaminant	Feed	Final Concentrate	Composite Permeate	Removal Efficiency, %*
Total Dissolved Solids (mg/l)	14,240	59,570	226	98.4
Suspended Solids (mg/l)	27	113	< 4	>85.2
Oil and Grease (mg/l)	8	< 4	< 4	>50.0
TOC (mg/l)	66	240	8	87.9
COD (mg/l)	511	3,320	6	98.8
BOD_5 (mg/l)	11	60	4	63.6
Surfactants (mg/l)	1.3	6.6	0.2	84.6
Iron (mg/l)	2.7	6.6	< 1	>62.9
Lead (mg/l)	0.5	1.5	< 0.5	-
Color (units)	200	700	5	97.5
Turbidity (NTU)	5.0	7.1	0.34	93.2
pH	7.0	6.6	6.5	-
Conductivity (µmhos/cm)	14,500	64,000	320	97.8

$$\text{*Removal Efficiency, R} = \frac{\text{Concentration of Feed - Concentration of Composite Permeate}}{\text{Concentration of Feed}} \times 100$$

Ozonation

Ozonation experiments were performed only with the depth filter carbon-treated effluent since the COD (6 mg/ℓ) of the reverse osmosis permeate was below BATEA standards. Two Type A and two Type B tests were conducted with the composite effluent from the first of the partial carbon column runs described above. The test conditions are given in Table 37.

The results for ozonation of SEC carbon effluent are shown in Figures 36 through 39 for runs A-1, A-2, B-1, and B-2, respectively. For both Type A runs, the dissolved ozone concentration increased rapidly to a plateau value indicating that the removal of TOC was limited by the rate of reaction between dissolved ozone and dissolved organics rather than by mass transfer.

TABLE 37. TEST CONDITIONS DURING OZONATION OF SEC CARBON COLUMN EFFLUENT

Test Type	Run	Temperature (°C)	pH	UV Light
A	1	30	9	off
	2	30	5	off
B	1	30	9	off
	2	30	5	off

A significant difference exists in the initial TOC concentrations for these two runs (21 and 39 mg/ℓ). This may have been the result of biological activity in the liquid storage container which was not refrigerated. At both pH's the initial decrease in TOC is rapid, but at pH 5 the TOC levels off at about 13 mg/ℓ, whereas the TOC continues to decrease at pH 9.

There is some scatter in the measured TOC values for the Type B run at pH 5. Based on the rather uncertain dashed line shown in Figure 39, the ozone utilization efficiency for organics oxidation is only 14%. This can be attributed to the very slow rate of reaction at low pH and the predominance of non-productive ozone decomposition.

The results for pH 9 are shown in Figure 38. The TOC decreased much more rapidly at pH 9 than at pH 5. The change in slope for the theoretical curve (triangles) results from a change in ozone flow rate from 0.028 m^3/hr (1 CFH) to 0.008 m^3/hr (0.3 CFH). The actual TOC data points were correlated with a straight line changing slope at the same point. Based on an extrapolation of the theoretical curve, the ozone utilization efficiency for reduction of the TOC to 5 mg/ℓ is 45%. For this waste, ozonation at high pH

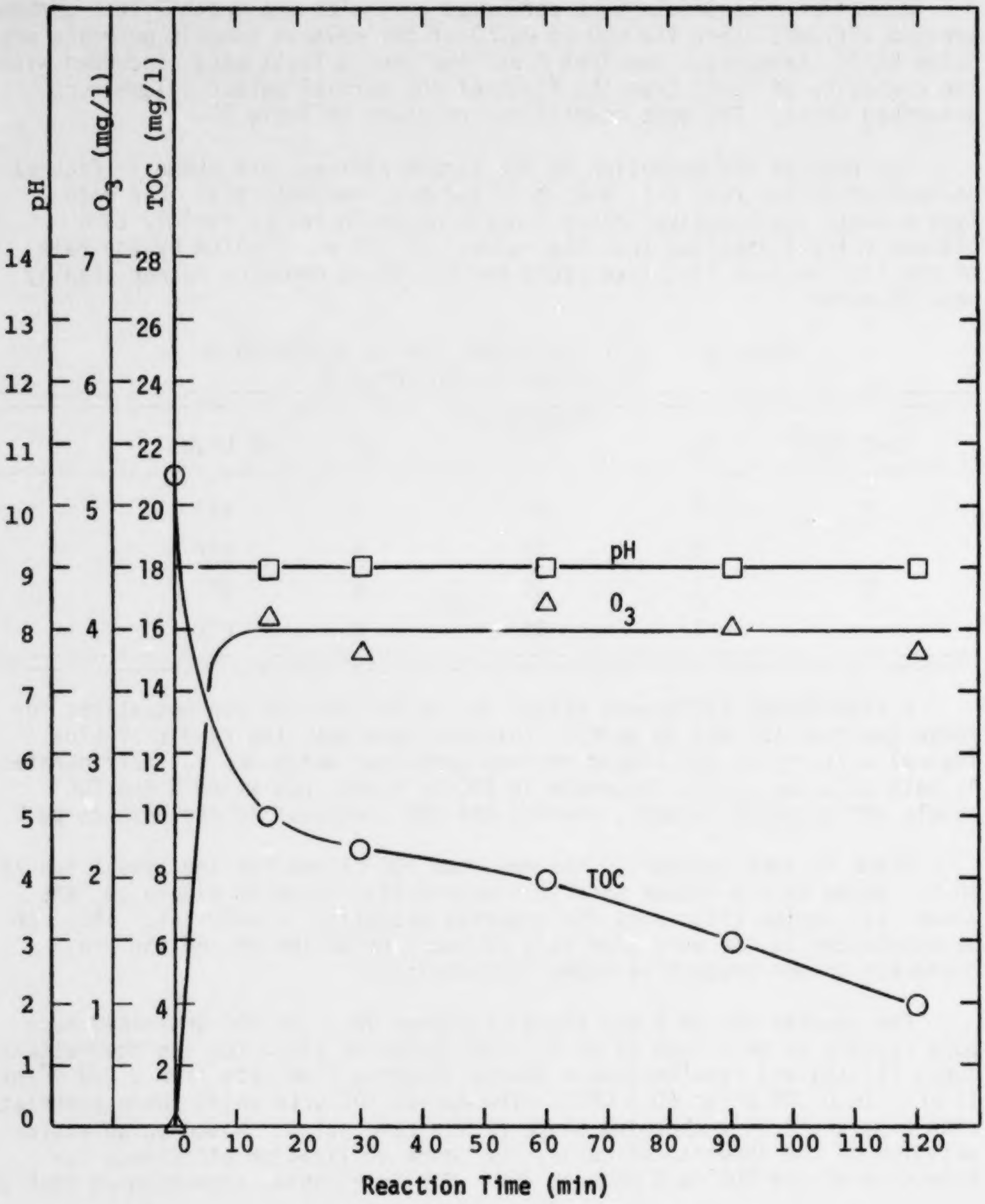

Figure 36. Ozonation of secondary treated emulsion crumb carbon effluent at 30°C and pH 9 without UV light.

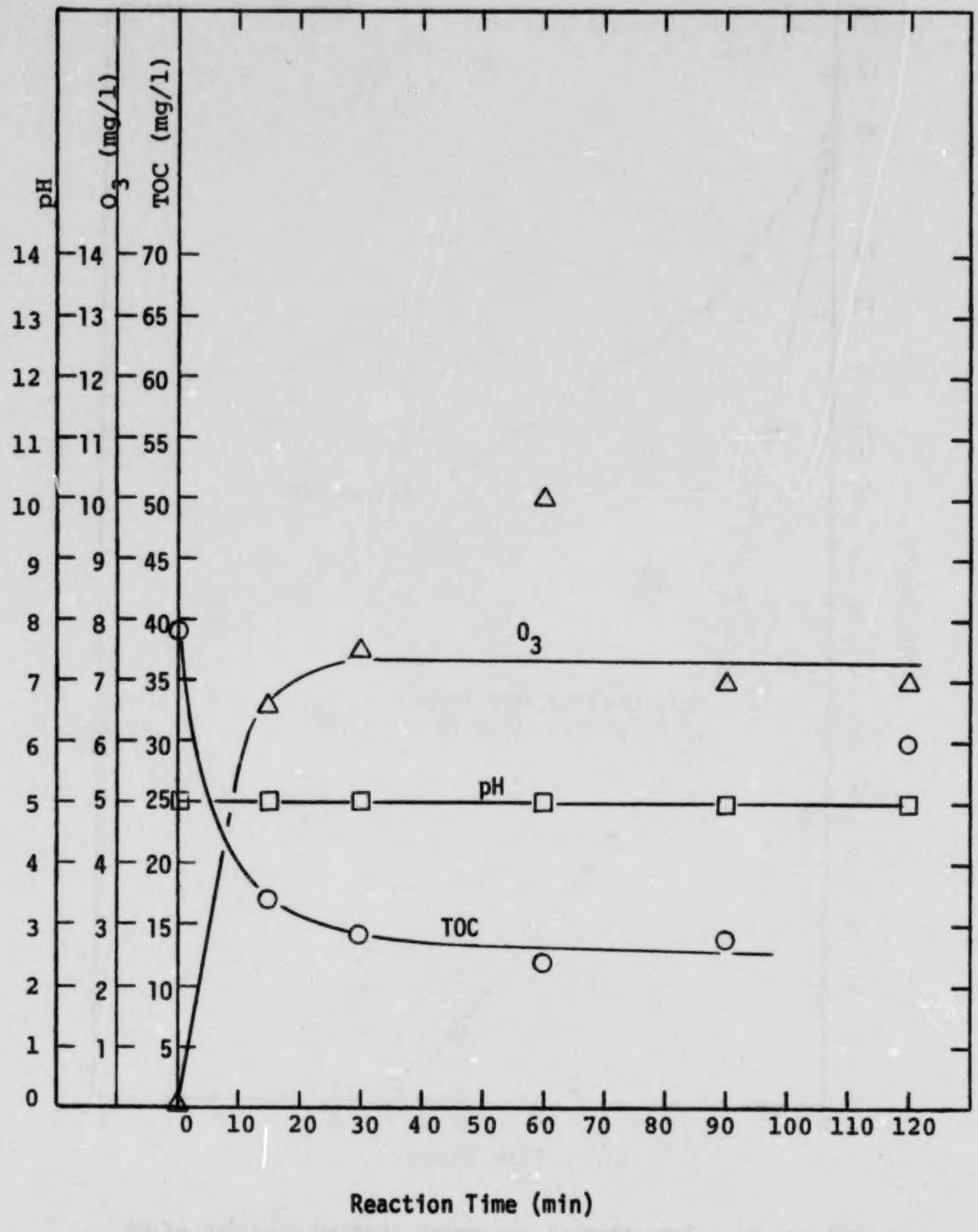

Figure 37. Ozonation of secondary treated emulsion crumb carbon effluent at 30°C and pH 5 without UV light.

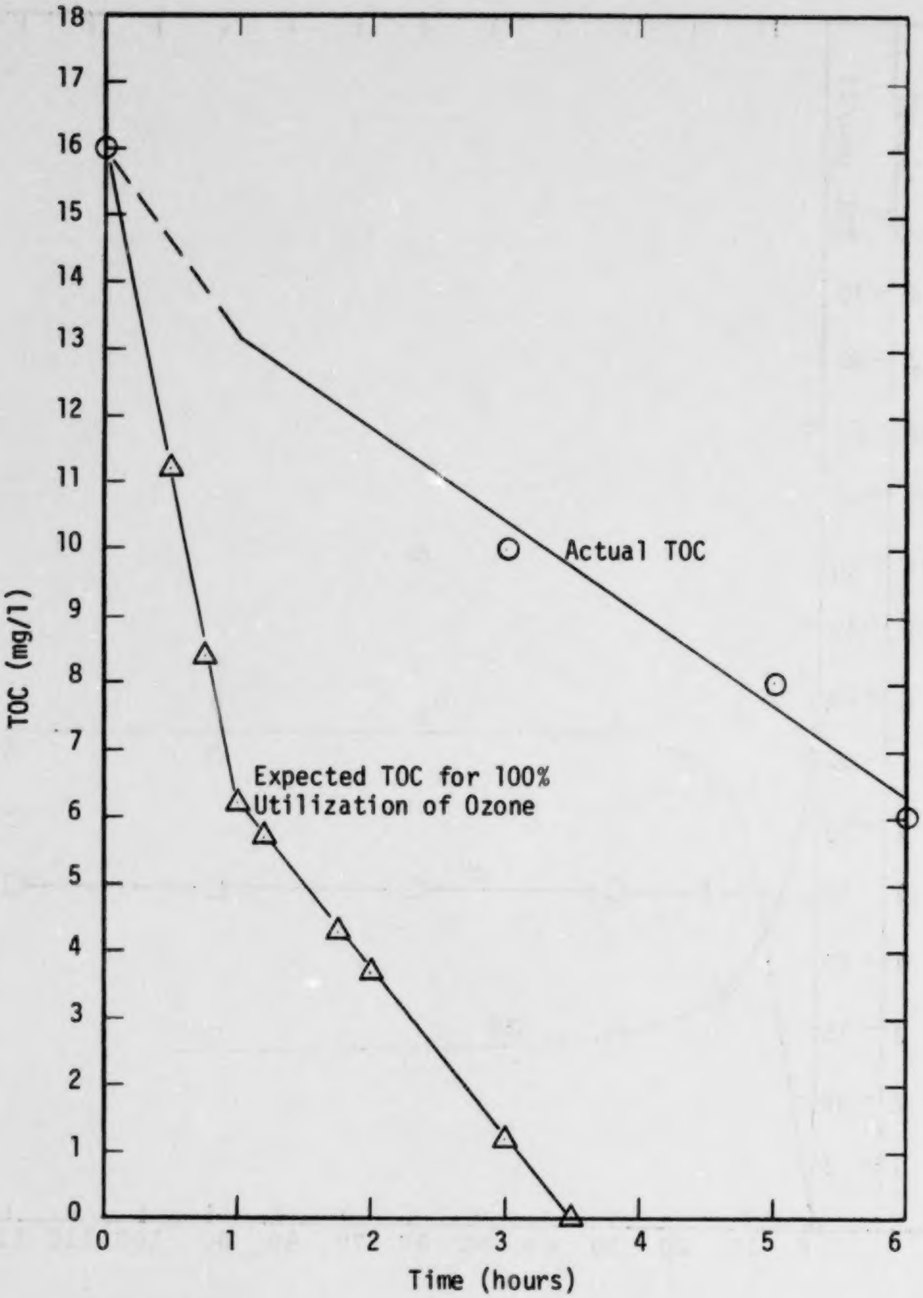

Figure 38. Ozonation of secondary treated emulsion crumb carbon effluent at 30°C and pH 9 without UV light (type B).

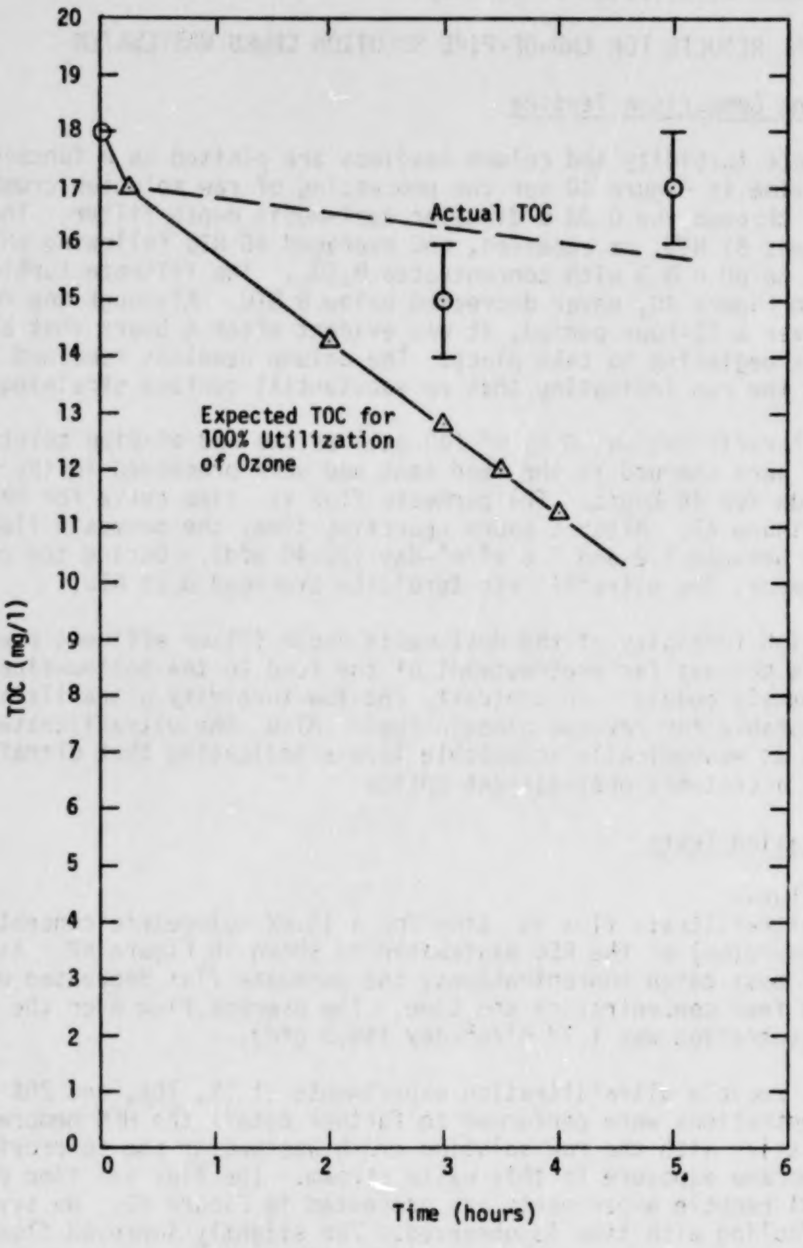

Figure 39. Ozonation of secondary treated emulsion crumb carbon effluent at 30^{o}C and pH 5 without UV light (type B).

is preferred both from the standpoint of reaction rate and from the standpoint of ozone utilization efficiency.

EXPERIMENTAL RESULTS FOR END-OF-PIPE SOLUTION CRUMB WASTEWATER

Pretreatment Comparison Testing

Filtrate turbidity and column headloss are plotted as a function of operating time in Figure 40 for the processing of raw solution crumb (RSC) wastewater through the 0.05 m diameter dual-media depth filter. The feed turbidity was 81 NTU, as received, and averaged 40 NTU following pH adjustment to pH = 8.3 with concentrated H_2SO_4. The filtrate turbidity, as observed in Figure 40, never decreased below 8 NTU. Although the run extended over a 12-hour period, it was evident after 5 hours that breakthrough was beginning to take place. The column headloss remained stable throughout the run indicating that no substantial surface straining occurred.

For ultrafiltration, 0.15 m^3 (40 gal) of the end-of-pipe solution crumb wastewater were charged to the feed tank and were processed in the total-recycle mode for 46 hours. The permeate flux vs. time curve for this test is shown in Figure 41. After 5 hours operating time, the permeate flux stabilized between 1.2 and 1.6 m^3/m^2-day (30-40 gfd). During the course of the experiment, the ultrafiltrate turbidity averaged 0.25 NTU.

The high turbidity of the dual-media depth filter effluent precludes the use of this process for pretreatment of the feed to the hollow-fine-fiber reverse osmosis module. In contrast, the low turbidity ultrafiltrate was quite acceptable for reverse osmosis feed. Also, the ultrafiltrate flux stabilized at economically acceptable levels indicating that ultrafiltration is an acceptable pretreatment option.

Ultrafiltration Tests

Membrane Flux--

The ultrafiltrate flux vs. time for a 15.6X volumetric concentration (93.6% conversion) of the RSC wastewater is shown in Figure 42. As is typical of most batch concentrations, the permeate flux decreased with both increasing feed concentration and time. The average flux over the 14-hour batch concentration was 1.77 m^3/m^2-day (44.3 gfd).

Total recycle ultrafiltration experiments at 5X, 10X, and 20X volumetric feed concentrations were performed to further detail the HFM membrane flux characteristics with the raw solution crumb wastewater and to provide prolonged membrane exposure to this waste stream. The flux vs. time data for these total recycle experiments are presented in Figure 43. No severe membrane fouling with time is observed. The slightly improved flux for the 10X feed sample as compared to the 5X feed after ~9 hours recirculation is not readily explainable.

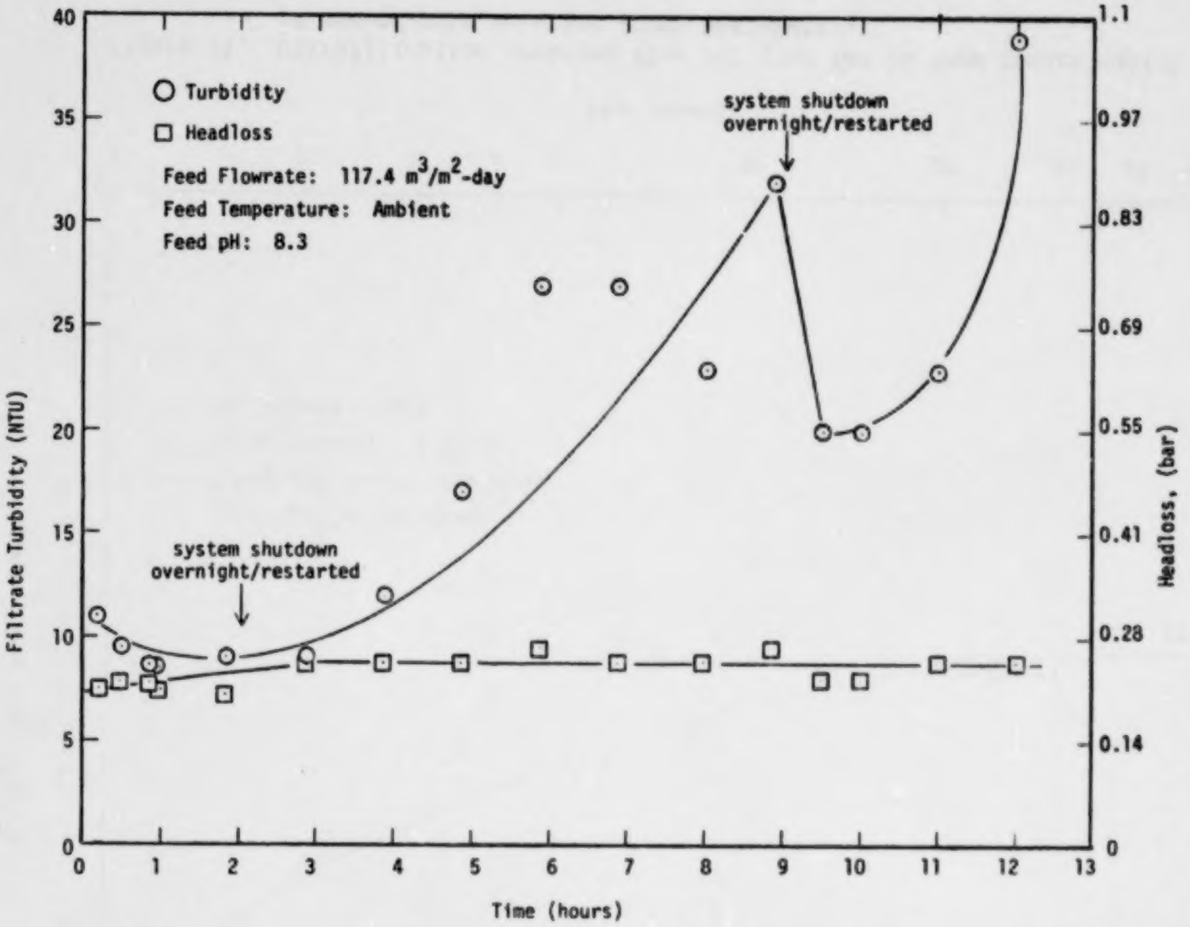

Figure 40. Filtrate turbidity and column headloss vs. time for dual-media depth filtration of end-of-pipe solution crumb wastewater, 0.05 m diameter column.

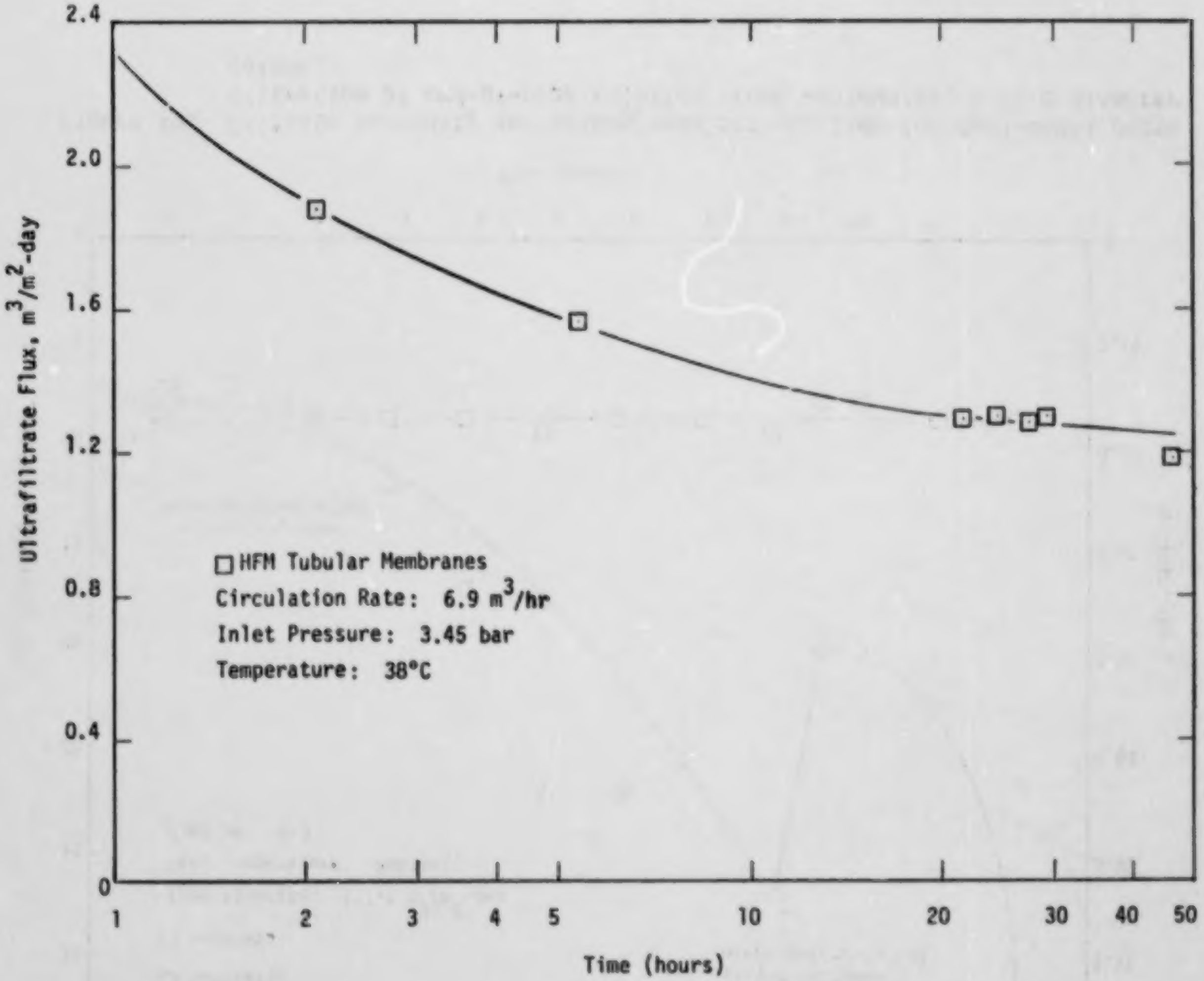

Figure 41. Ultrafiltration membrane flux vs. time for 1X feed concentration of end-of-pipe solution crumb wastewater.

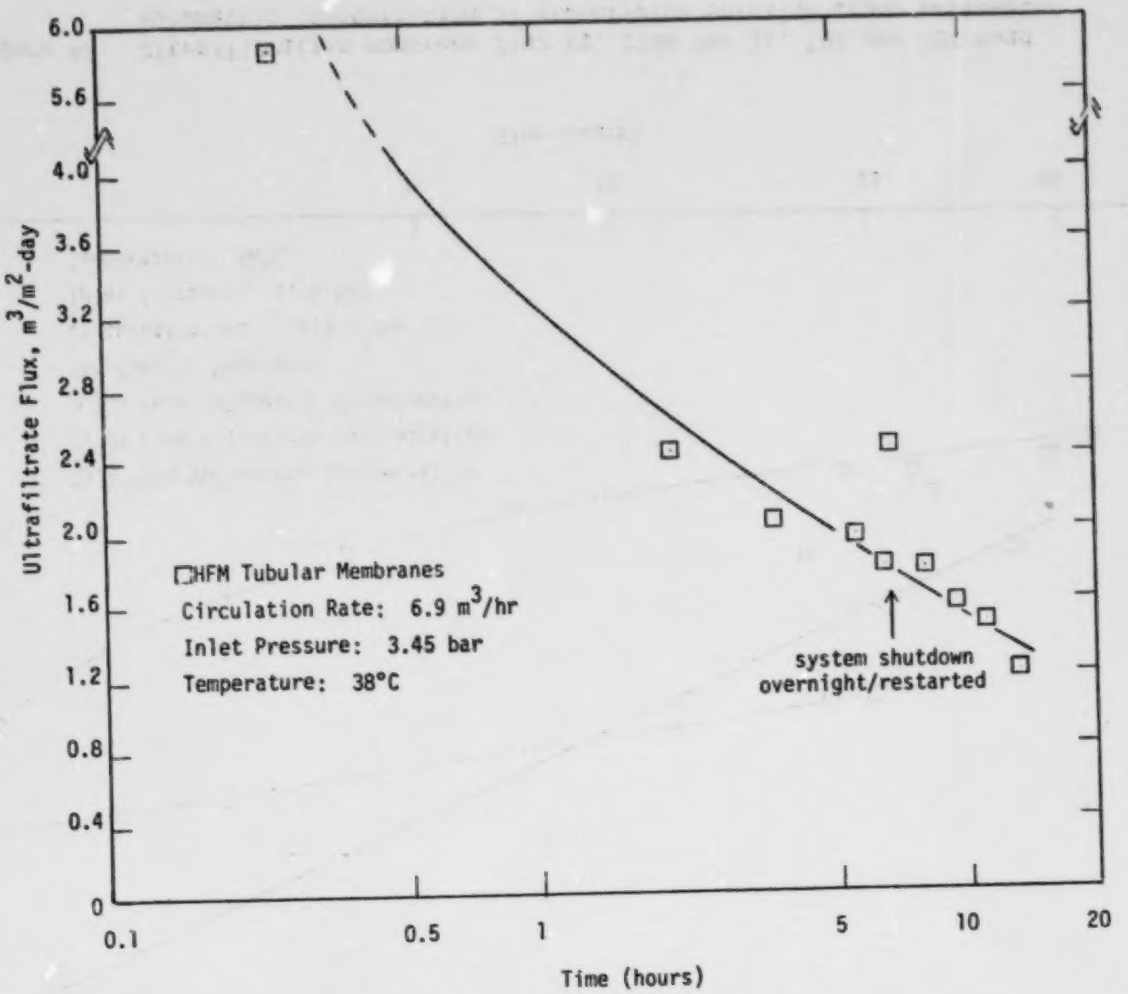

Figure 42. Ultrafiltration membrane flux vs. time for batch concentration of end-of-pipe solution crumb wastewater.

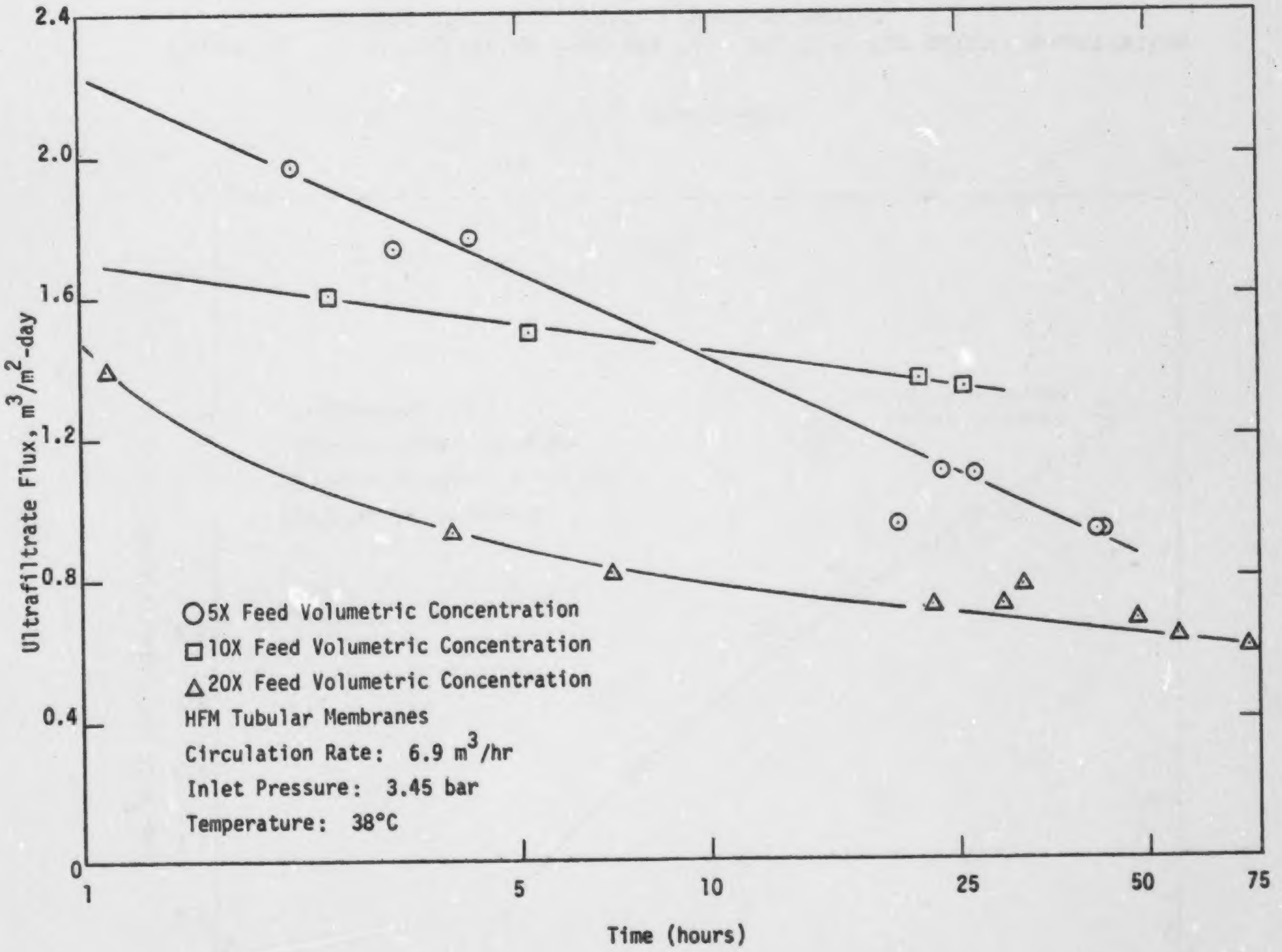

Figure 43. Ultrafiltration membrane flux vs. time for 5X, 10X and 20X feed volumetric concentration of end-of-pipe solution crumb wastewater.

Membrane Rejection--

Feed, composite permeate, and final concentrate contaminant analyses are presented in Table 38 for ultrafiltration of the raw solution crumb wastewater. The HFM membrane rejections for BOD_5, COD, and TOC were 65%, 29%, and 15%, respectively. The overall rejection for oil and grease was 61%. A comparison of the composite ultrafiltrate analyses and the effluent guideline standards is presented in Table 39. It does not appear that ultrafiltration alone can successfully treat the raw solution crumb wastewater to the degree required to meet either the BPCTCA or BATEA standards.

TABLE 39. COMPARISON OF RSC ULTRAFILTRATE WITH EFFLUENT GUIDELINES FOR SOLUTION CRUMB MANUFACTURING WASTES

Assay	Composite Ultrafiltrate	BPCTCA	BATEA
COD (mg/ℓ)	444	245	130
BOD_5 (mg/ℓ)	30	25	5
Suspended Solids (mg/ℓ)	<4	40	10
Oil and Grease (mg/ℓ)	11	10	5

Membrane Flux Recovery--

Table 40 presents the flux recovery data and accumulated operating time for the ultrafiltration membranes used to treat the raw solution crumb wastewaters. The data are also summarized for all previous exposures of these membranes to synthetic rubber manufacturing wastewaters. Throughout nearly 300 hours of exposure to these wastes, no membrane degradation due to environmental attack is evident.

Reverse Osmosis Tests

Module Productivity--

The reverse osmosis module employed during the processing of the end-of-pipe solution crumb ultrafiltrate was a duPont B-9 polyamide hollow-fine-fiber permeator. This module is well-suited for the range of dissolved solids (800-1200 mg/ℓ) in the ultrafiltrate. The B-9 operates with a feed pressure of 27.6 bar (400 psig).

The B-9 permeate flow rate is shown in Figure 44 as a function of volumetric feed concentration for batch concentration to 17.3X. As expected, the productivity of the B-9 module declined gradually with the increase in volumetric feed concentration. This productivity loss is associated with the increase in the feed osmotic pressure which results in the reduction of the net driving pressure across the membrane. The flux level at 10X was, however, still 6.34 m^3/day (1.15 gpm) which is an economically attractive

TABLE 38. CONTAMINANT ANALYSES FOR ULTRAFILTRATION OF END-OF-PIPE SOLUTION CRUMB WASTEWATER

Contaminant	pH Adjusted Feed	Final Concentrate	Composite Permeate	Removal Efficiency, %*
Total Dissolved Solids (mg/l)	1060	1460	1050	---
Suspended Solids (mg/l)	123	2740	<4	>96.7
Oil and Grease (mg/l)	28	105	11	60.7
TOC (mg/l)	144	1100	122	15.3
COD (mg/l)	625	2660	444	29.0
BOD_5 (mg/l)	86	200	30	65.1
Surfactants (mg/l)	0.66	1.8	0.52	21.2
Iron (mg/l)	3.4	58	<1.0	>70.6
Lead (mg/l)	<1.0	<1.0	<1.0	---
Color (units)	100	4000	80	20.0
Turbidity (NTU)	55	255	0.55	99.0
pH	8.4	8.3	8.3	---
Conductivity (μmhos/cm)	1230	(1900)	1300	---

*Removal Efficiency, $r = \frac{\text{concentration of feed - concentration of composite permeate}}{\text{concentration of feed}} \times 100$

Note: ( ) indicates suspected error in analysis

TABLE 40. FLUX RECOVERY AND ACCUMULATED OPERATING TIME FOR TUBULAR HFM MEMBRANES OPERATING ON SYNTHETIC RUBBER WASTEWATERS

Wastewater Description	Accumulated Operating Time (hours)	Water Flux before "Spongeball" (m^3/m^2-day)	Water Flux after "Spongeball" (m^3/m^2-day)
New Membranes	0	10.4	---
End-of-pipe Emulsion Crumb	76	7.96	11.1
End-of-pipe Latex	87	2.40	10.7
End-of-pipe Solution Crumb			
a) 1X Recycle	133	7.72	11.8
b) Batch Concentration	147	5.68	12.8
c) 5X Recycle	192	8.44	14.3
d) 10X Recycle	220	12.4	14.6
e) 20X Recycle	292	8.52	11.1

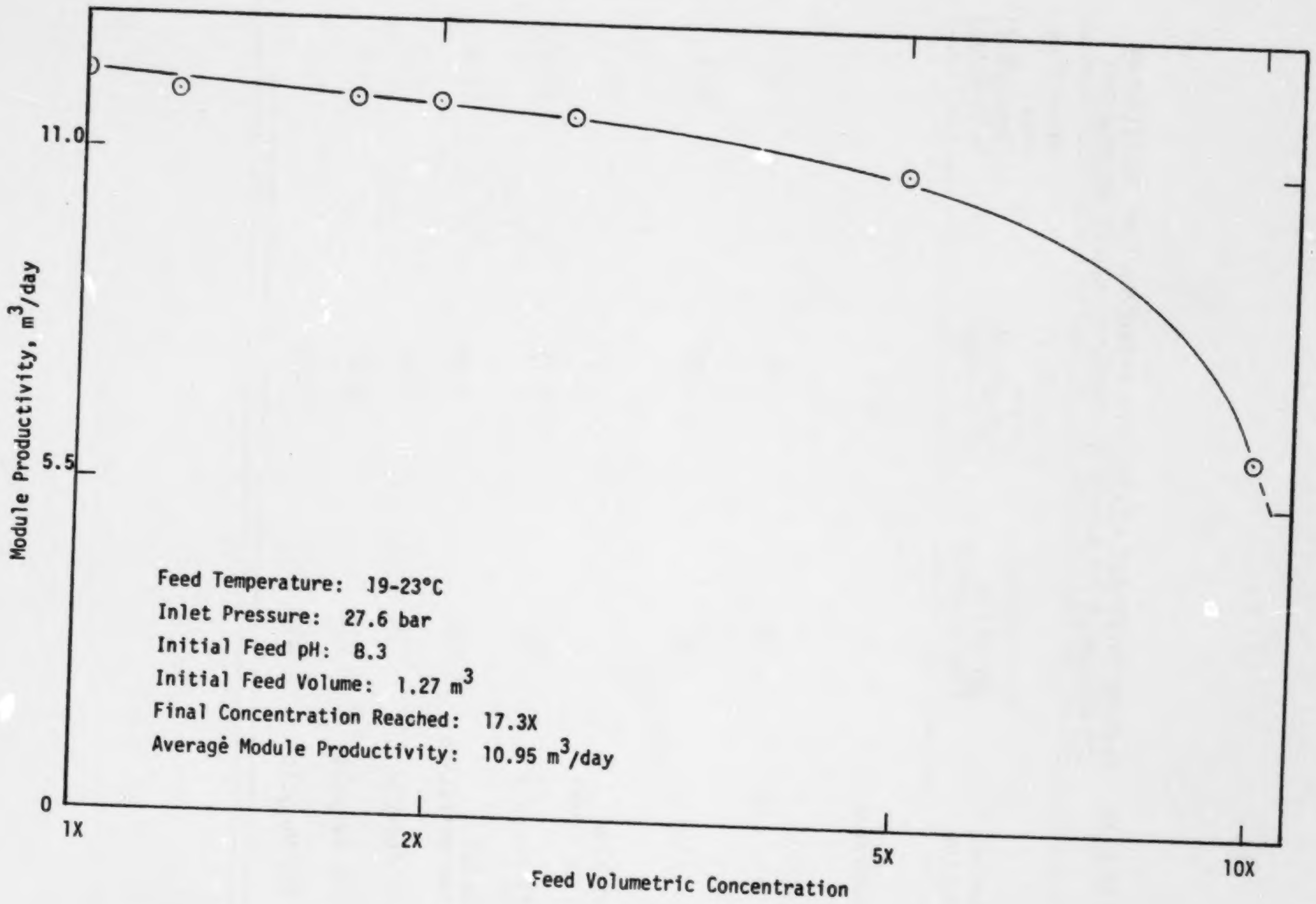

Figure 44. Productivity vs. feed volumetric concentration for duPont B-9 processing of end-of-pipe solution crumb ultrafiltrate.

productivity for this type of module. The average module productivity for concentration to 17.3X was 10.95 m^3/day (1.99 gpm). A productivity of this magnitude should make reverse osmosis a viable unit process for treatment of the raw solution crumb ultrafiltrate.

The B-9 module was also exposed to the raw solution crumb ultrafiltrate for extended time periods during total recycle experiments at 1X and 5X volumetric feed concentrations. The CA spiral-wound module was operated in series with the B-9 module during the 1X recycle test only. Although not readily explainable, the narrow pH range for the CA module (pH 4-6) could not be maintained with this wastewater without constant pH adjustment; therefore, testing of the CA module was discontinued.

The permeate flow rates during these total recycle experiments are presented as a function of operating time in Figure 45. Except for minor fluctuations due to a temperature increase following system start-up(s), the permeate flow levels were stable for the course of the experiments. This indicates the absence of membrane fouling during these tests.

The results of the standard NaCl performance tests presented in Table 41 also indicate the favorable and consistent performance of the CA and B-9 modules. Productivity of the CA module increased 8%, while the B-9 module productivity decreased by 2%. Module rejection decreased 1% and 2.5% for the CA and B-9 modules, respectively. These data indicate little change in module performance after exposure to this waste stream.

Module Rejection--

Feed, point and composite permeate, and final concentrate analyses for the batch concentration of the RSC ultrafiltrate are presented in Table 42. Those assays which are in common with the Development Document guidelines are further summarized in Table 43. The reverse osmosis permeate meets essentially all BPCTCA and BATEA standards. The oil and grease level in the permeate is, however, in excess of the BATEA standard by 2 mg/ℓ.

TABLE 43. COMPARISON OF RSC REVERSE OSMOSIS PERMEATE WITH EFFLUENT GUIDELINES FOR SOLUTION CRUMB MANUFACTURING WASTES

Assay	Composite Reverse Osmosis Permeate	BPCTCA	BATEA
COD (mg/ℓ)	36	245	130
BOD_5 (mg/ℓ)	4	25	5
Suspended Solids (mg/ℓ)	nil	40	10
Oil and Grease (mg/ℓ)	7	10	5

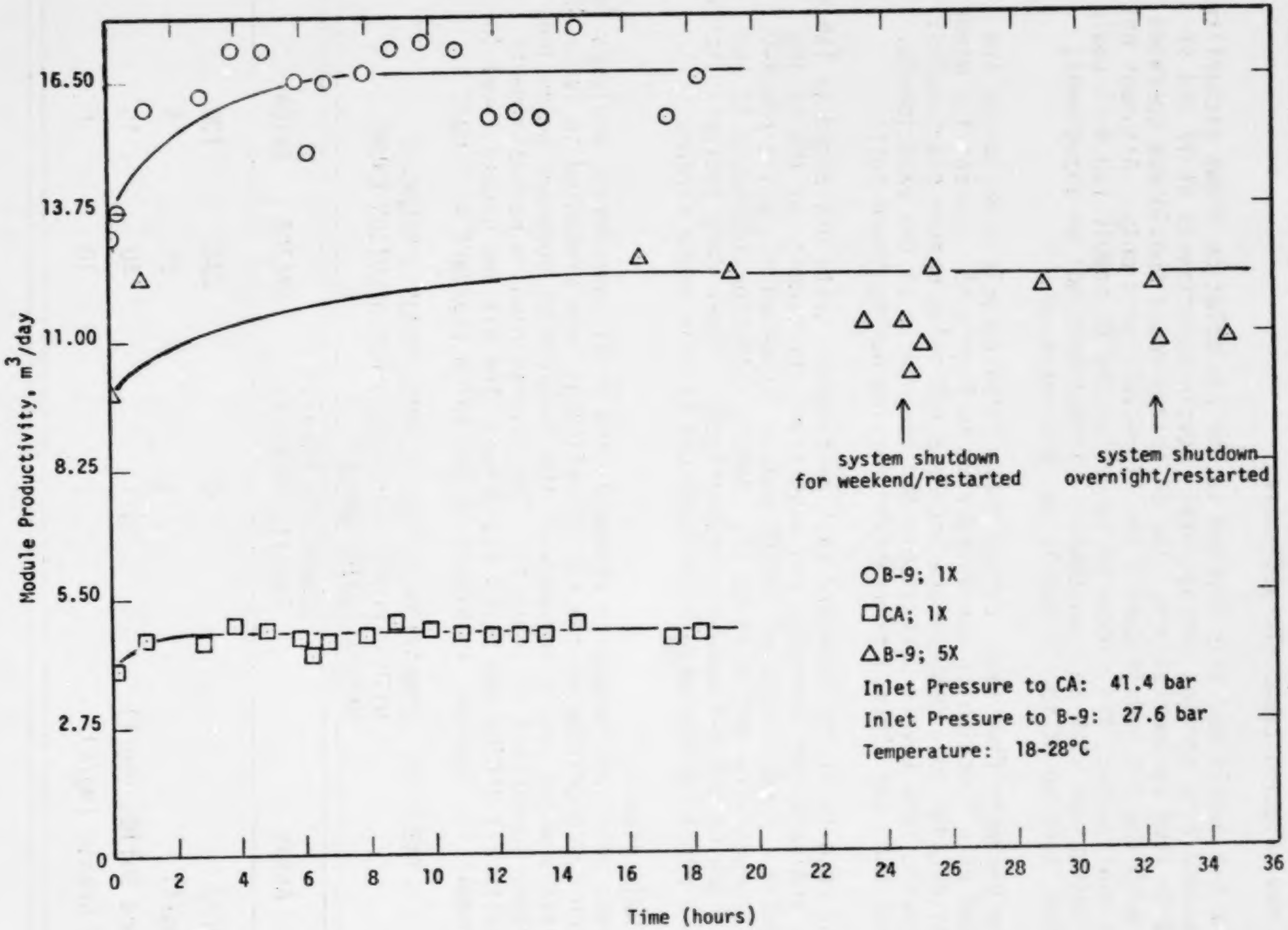

Figure 45. Reverse osmosis module productivity vs. time for total recycle life tests with end-of-pipe solution crumb ultrafiltrate.

TABLE 41. HISTORY OF SALT REJECTIONS FOR REVERSE OSMOSIS MODULES DURING PROCESSING OF END-OF-PIPE SOLUTION CRUMB ULTRAFILTRATE

Module	Cumulative Operating Time (hrs)	Feed Concentration NaCl (ppm)	Temperature (°C)	Permeate Flowrate m^3/day	Feed Flowrate m^3/day	Conversion %	Rejection %	Intrinsic Rejection	Remarks
Roga 4160 HR Spiral-Wound Cellulose-Acetate (CA)	226	4700	27	3.87	28.67	13.4	93.0	0.933	Following secondary treated emulsion crumb DMDF filtrate total recycle runs
	244	4800	28	4.20	28.61	14.7	92.1	0.924	Following end-of-pipe solution crumb ultrafiltrate 1X total recycle run
duPont B-9 Hollow-Fine-Fiber Polyamide	9.2	5200	26	12.21	24.74	49.3	95.9	0.969	Following preliminary test with end-of-pipe emulsion crumb ultrafiltrate
	11.8	7050	24	9.70	28.72	33.8	92.6	0.935	Following end-of-pipe solution crumb ultrafiltrate batch concentration
	30	5560	27	12.7	24.42	52.0	91.4	0.936	Following 1X recycle
	67	4950	28	12.0	28.34	42.3	93.0	0.945	Following 5X recycle

TABLE 42. CONTAMINANT ANALYSES FOR REVERSE OSMOSIS (DUPONT B-9) PROCESSING OF END-OF-PIPE SOLUTION CRUMB ULTRAFILTRATE

Contaminant	Feed (Composite Ultrafiltrate)	Final Concentrate	1X Permeate	5X Permeate	Composite Permeate	Removal Efficiency, %*
Total Dissolved Solids (mg/l)	1,050	36,800	57	215	141	86.6
Suspended Solids (mg/l)	< 4	---	---	---	---	---
Oil and Grease (mg/l)	11	49	---	---	7	36.4
TOC (mg/l)	122	4,200	6	12	10	91.8
COD (mg/l)	444	11,300	< 5	40	36	91.9
BOD_5 (mg/l)	30	84	---	---	4	86.7
Surfactants (mg/l)	0.52	24.4	---	---	0.4	23.1
Iron (mg/l)	< 1.0	4.5	---	---	< 1.0	---
Lead (mg/l)	< 1.0	1.3	---	---	< 1.0	---
Color (units)	80	2,000	---	---	5	93.8
Turbidity (NTU)	0.55	5.3	0.1	0.1	0.52	5.5
pH	8.3	8.3	9.2	9.2	9.1	---
Conductivity (μmhos/cm)	1,300	25,500	33	225	180	86.2

*Removal Efficiency, R = $\frac{\text{Concentration of feed - Concentration of composite permeate}}{\text{Concentration of feed}} \times 100$

Carbon Adsorption Tests

The equilibrium adsorption isotherm at 20°C for the raw solution crumb ultrafiltrate is shown in Figure 46. The data indicate that the Freundlich isotherm expression does not hold over the entire range of carbon dosages investigated. However, two straight lines - one for low carbon doses (0.02 to 0.2 g/ℓ), the other for high carbon doses (0.2 to 5 g/ℓ) - fit the isotherm data quite well. This suggests that the adsorption of organics from RSC ultrafiltrate proceeds via the following mechanism: A small number of strongly adsorbed organics are initially removed by the activated carbon. If additional adsorption sites are available (i.e., more carbon present), then a large number of moderately adsorbed organics are removed and the slope of the isotherm levels out.

The TOC breakthrough curve for carbon column treatment of raw solution crumb ultrafiltrate is shown in Figure 47. Effluent concentrations from each of the four columns are shown in this figure as a function of the volume of waste processed. The curve for column 1 approaches the feed concentration very quickly following the trend observed in the isotherm. Thus, column 1 removes the small portion of strongly adsorbed organics, while columns 2, 3, and 4 adsorb the moderately hydrophobic organics. The curve for column 4 indicates a TOC of 40 mg/ℓ (i.e., COD of ~120 mg/ℓ) at 42 liters processed. Processing beyond this point would exceed the BATEA guideline of 130 mg/ℓ COD in the effluent.

The required carbon dosage would be 1.22 kg/m³ (10,160 lbs/MM gal). This is a relatively high carbon dosage and would result in treatment costs of approximately $1.06/m³ ($4.00/1000 gal). At this cost, activated carbon treatment of the raw solution crumb ultrafiltrate may be economically unattractive.

Ozonation Tests

Raw Solution Crumb Ultrafiltrate--

Results for ozonation of raw solution crumb ultrafiltrate at high ozone dosages (Type A tests) are presented in Figures 48 and 49. Both tests were performed at 30°C and without UV irradiation. The test results plotted in Figure 48 were obtained at pH 9; the test results of Figure 49 at pH 5.

The dissolved ozone concentration in both runs increased to a plateau value during the first fifteen minutes and remained fairly constant thereafter. This indicates that the rate of TOC removal was limited by the rate of reaction between dissolved organics and dissolved ozone (i.e., reaction-rate limited) and was not mass-transfer limited. Comparison of Figures 48 and 49 indicates that ozonation at the higher pH would be preferred from the reaction rate point of view. At pH 9, the rate of organic oxidation was approximately twice that achieved at pH 5. After 90 minutes of ozonation at pH 9, the product water TOC stabilized at 30 mg/ℓ (COD ~90 mg/ℓ).

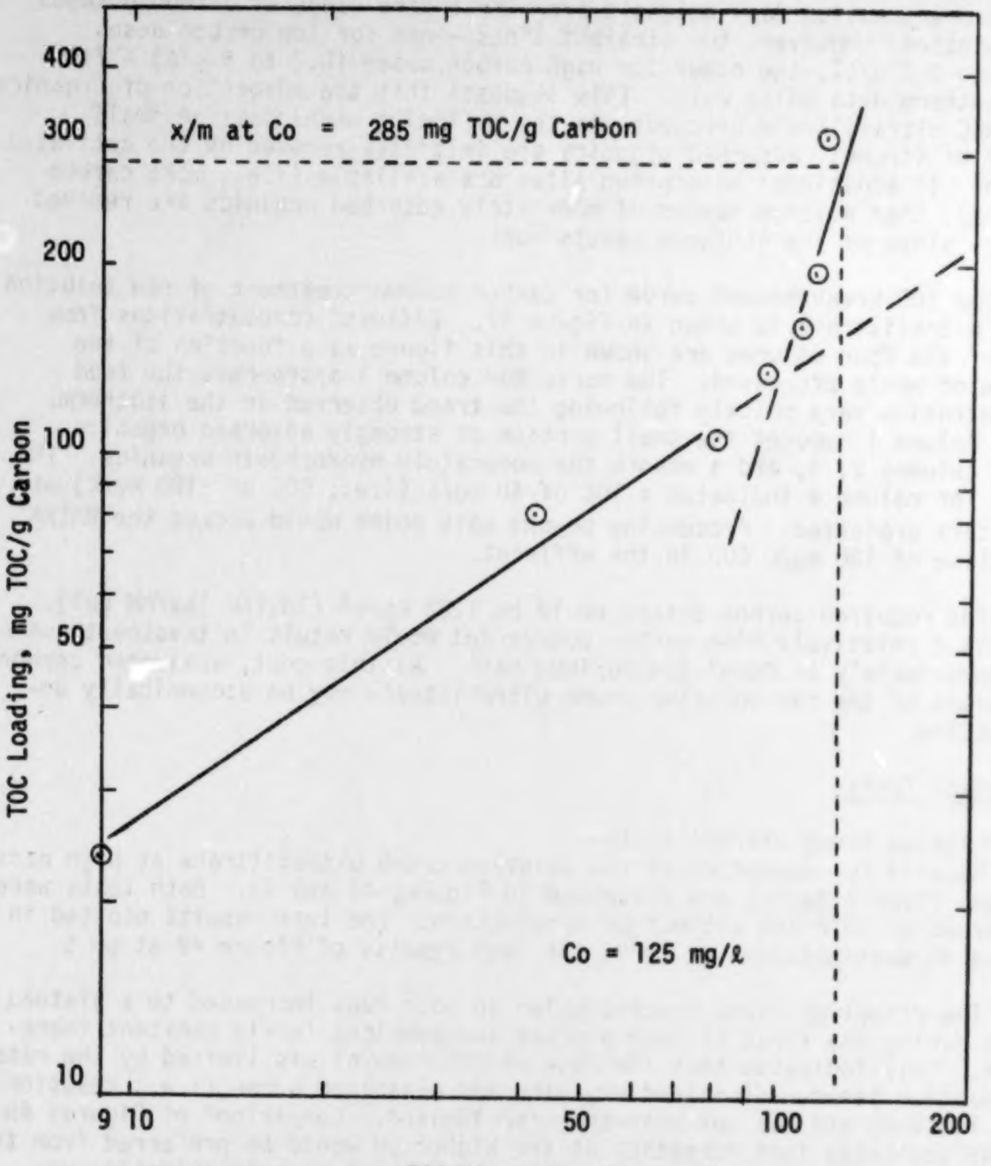

Figure 46. Equilibrium adsorption isotherm at 20°C for end-of-pipe solution crumb ultrafiltrate.

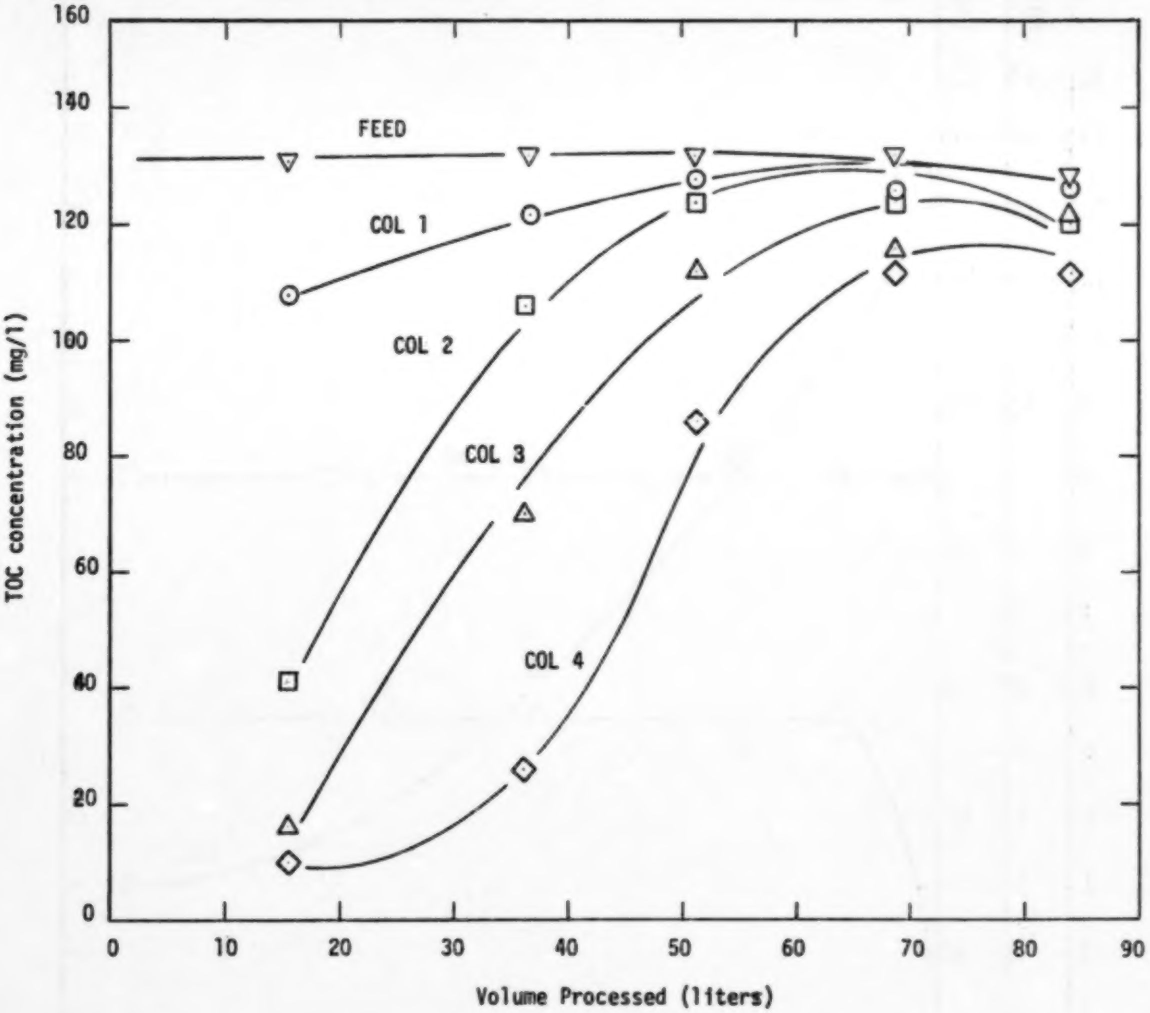

Figure 47. TOC breakthrough curves for carbon column treatment of end of pipe solution crumb ultrafiltrate.

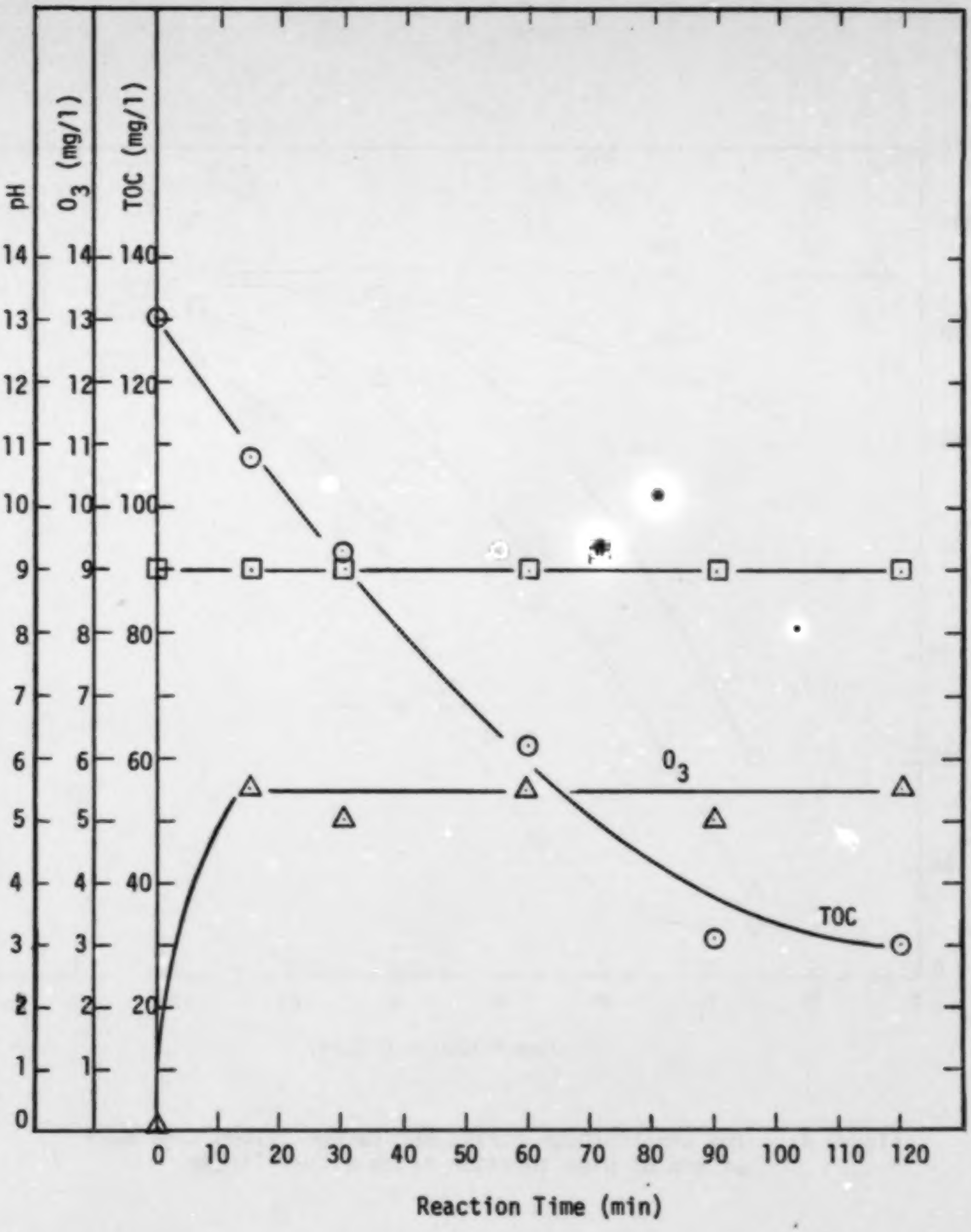

Figure 48. Ozonation of end-of-pipe solution crumb ultrafiltrate at 30°C and pH 9 without UV light.

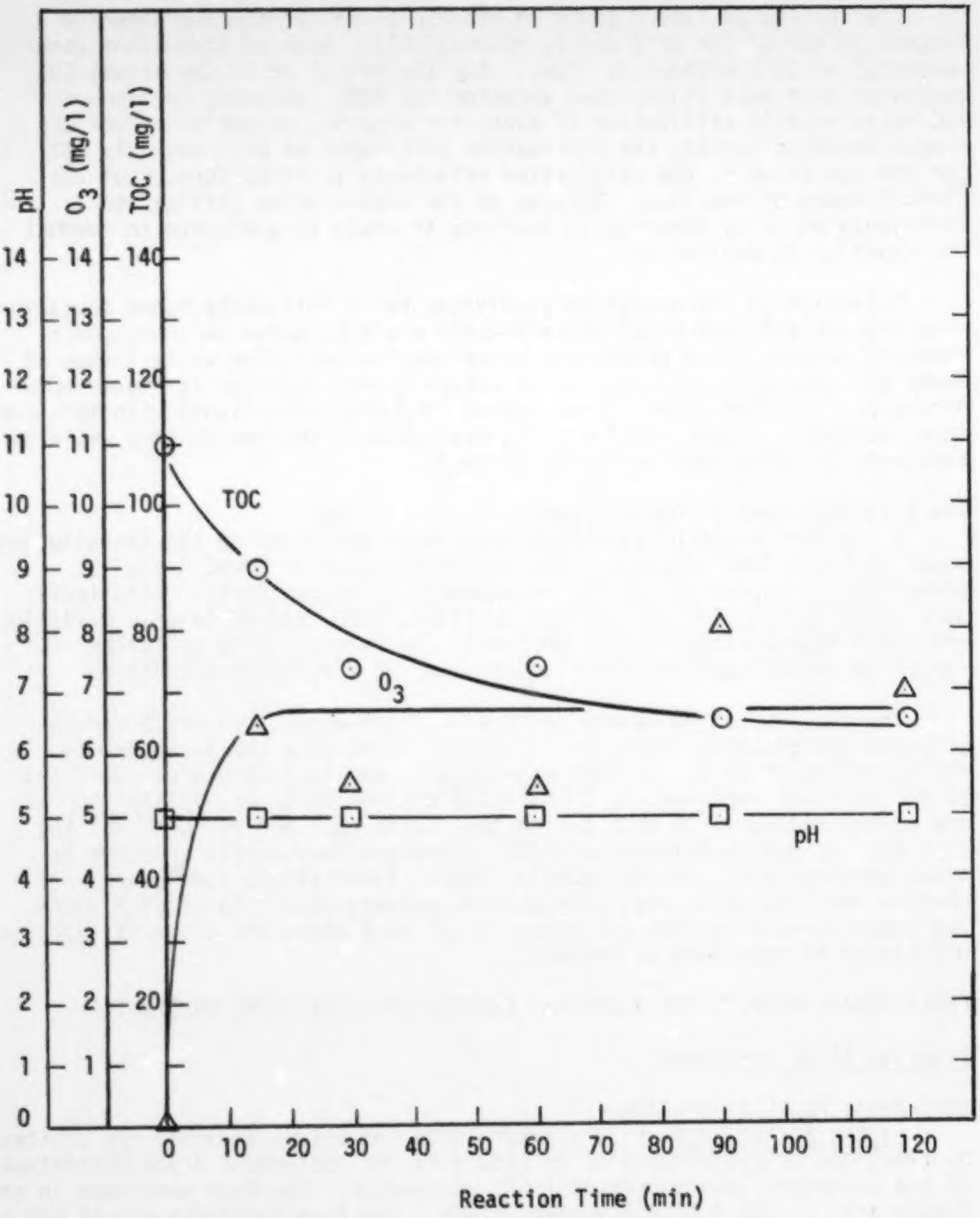

Figure 49. Ozonation of end-of-pipe solution crumb ultrafiltrate at 30°C and pH 5 without UV light.

The results of Type B tests on the RSC ultrafiltrate are shown in Figures 50 and 51 for pH 9 and 7, respectively. Both of these runs were conducted at 30°C without UV light. For the run at pH 9, the actual TOC decreased much more slowly than expected for 100% (assuming an ozone to TOC ratio of 8:1) utilization of ozone for organics oxidation. Over the 6-hour reaction period, the utilization efficiency at pH 9 was only 25%. For the run at pH 7, the utilization efficiency is ~100% throughout the first 5 hours of reaction. Because of the higher ozone utilization efficiency at pH 7, these tests indicate it would be preferred to conduct the reaction at neutral pH.

Selection of the operating conditions for a full-scale ozone contactor treating raw solution crumb ultrafiltrate would be based on an economic tradeoff between ozone generation power requirements (low ozone losses at lower pH) and multi-stage contactor volume (rapid reaction at higher pH). Although pH-related trends in ozonation have been established with this and other synthetic rubber manufacturing wastewaters, further testing would be necessary to fully develop design criteria.

Raw Solution Crumb Carbon Effluent--

A similar series of ozonation tests were performed on the raw solution crumb carbon column effluent. The Type A tests at pH 9 and 5 are presented in Figures B1 and B2, in Appendix B, respectively. Both tests were conducted at 30°C and without UV light. The rate of organic oxidation was again higher at the higher pH level. In fact, at pH 5 no further reduction in TOC occurred after the initial 30 minutes of ozonation.

The results of the Type B tests with the raw solution crumb carbon effluent are given in Figure B3 for ozonation at pH 9 and in Figure B4 for ozonation at pH 5. In both experiments, the temperature was 30°C and no UV light was employed. A substantial difference in the initial TOC of the carbon effluent, 44 mg/ℓ during the run at pH 9 and 110 mg/ℓ for the pH 5 run, is not readily explainable. However, very similar results to those obtained with the raw solution crumb ultrafiltrate (see above) reconfirm the conclusion that a compromise between ozonation at pH 9 where the reaction-rate is high and ozonation at pH 5 where the ozone utilization efficiency is high must be reached.

EXPERIMENTAL RESULTS FOR SECONDARY TREATED SOLUTION CRUMB WASTEWATER

Proposed BATEA Treatment

Dual-Media Depth Filtration--

Filter Performance--Filtrate turbidity and column headloss are plotted as functions of operating time in Figure 52 for dual-media depth filtration of the secondary solution crumb (SSC) wastewater. The data presented in this Figure are for the 0.05 m diameter column. The feed turbidity was 14 NTU as received and averaged 23 NTU during processing at a pH of 7.5. The filtrate

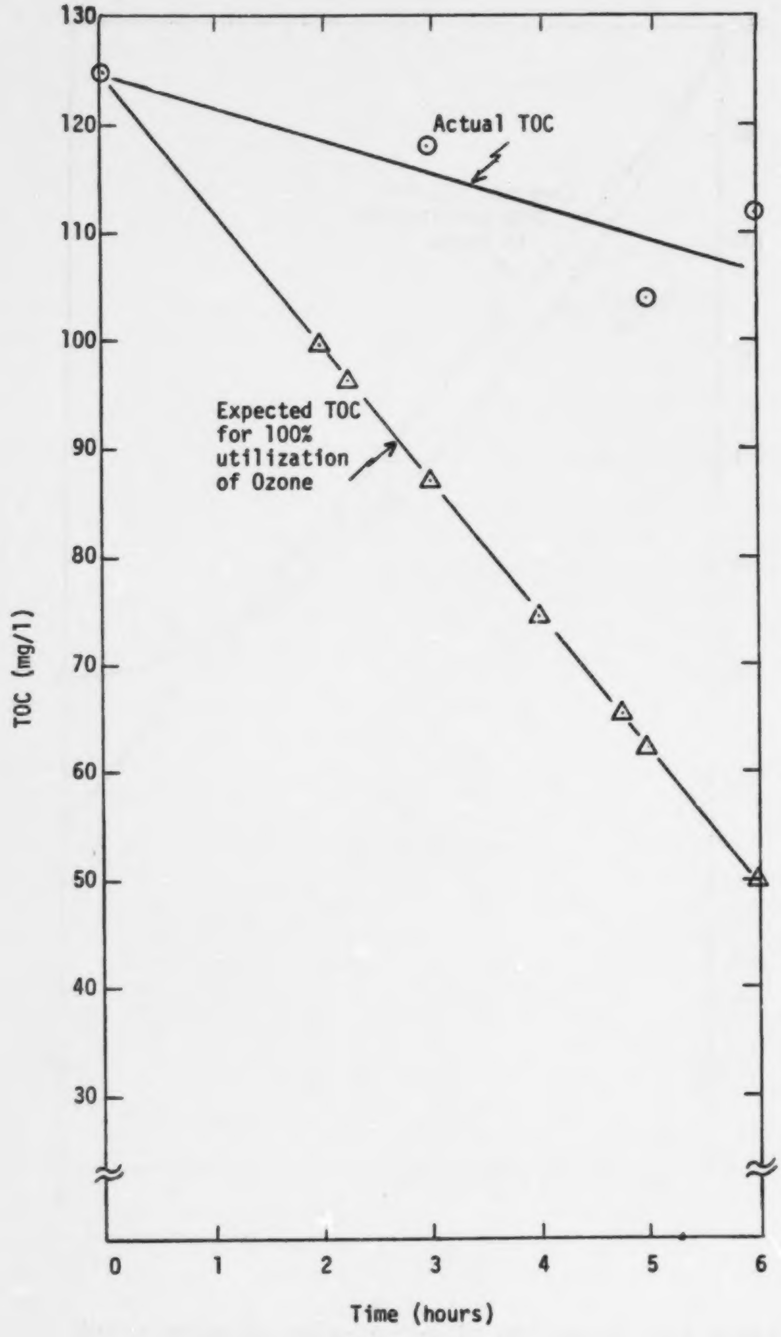

Figure 50. Ozonation of end-of-pipe solution crumb ultrafiltrate at 30°C and pH 9 without UV light (type B).

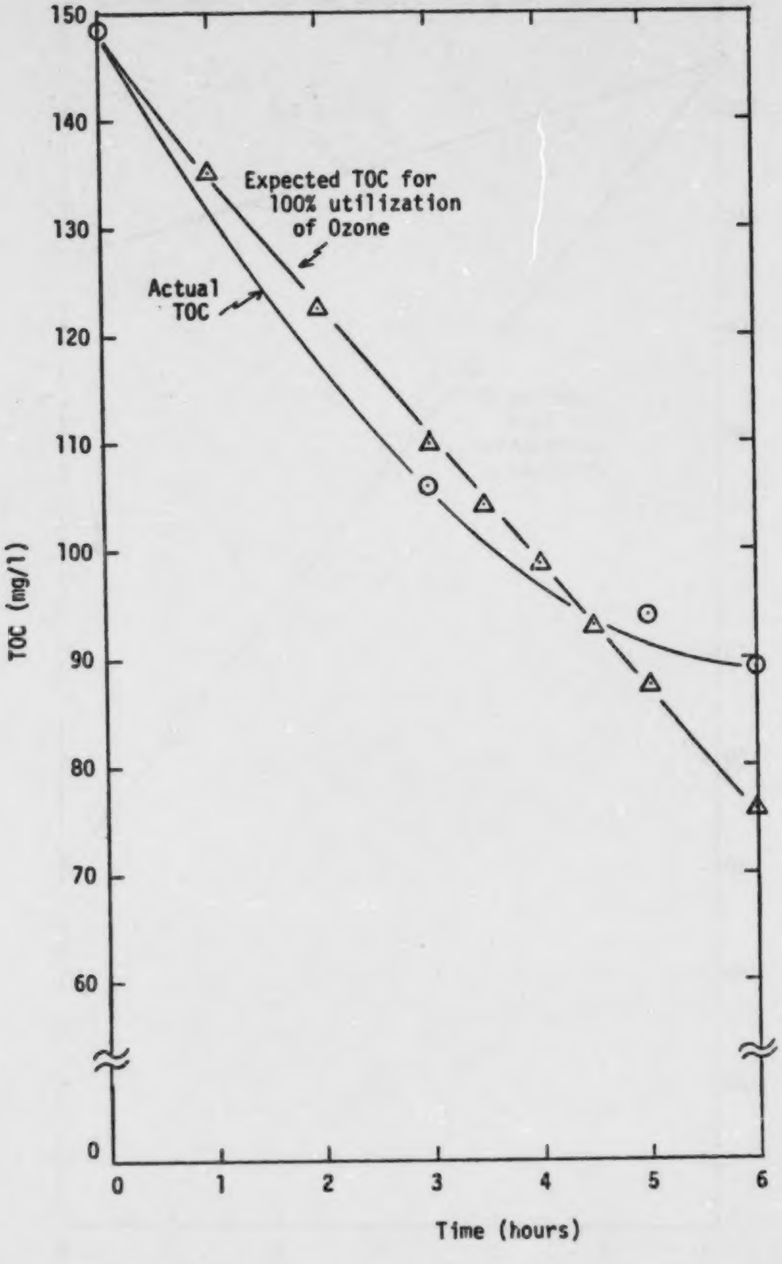

Figure 51. Ozonation of end-of-pipe solution crumb ultrafiltrate at 30^{o}C and pH 7 without UV light (type B).

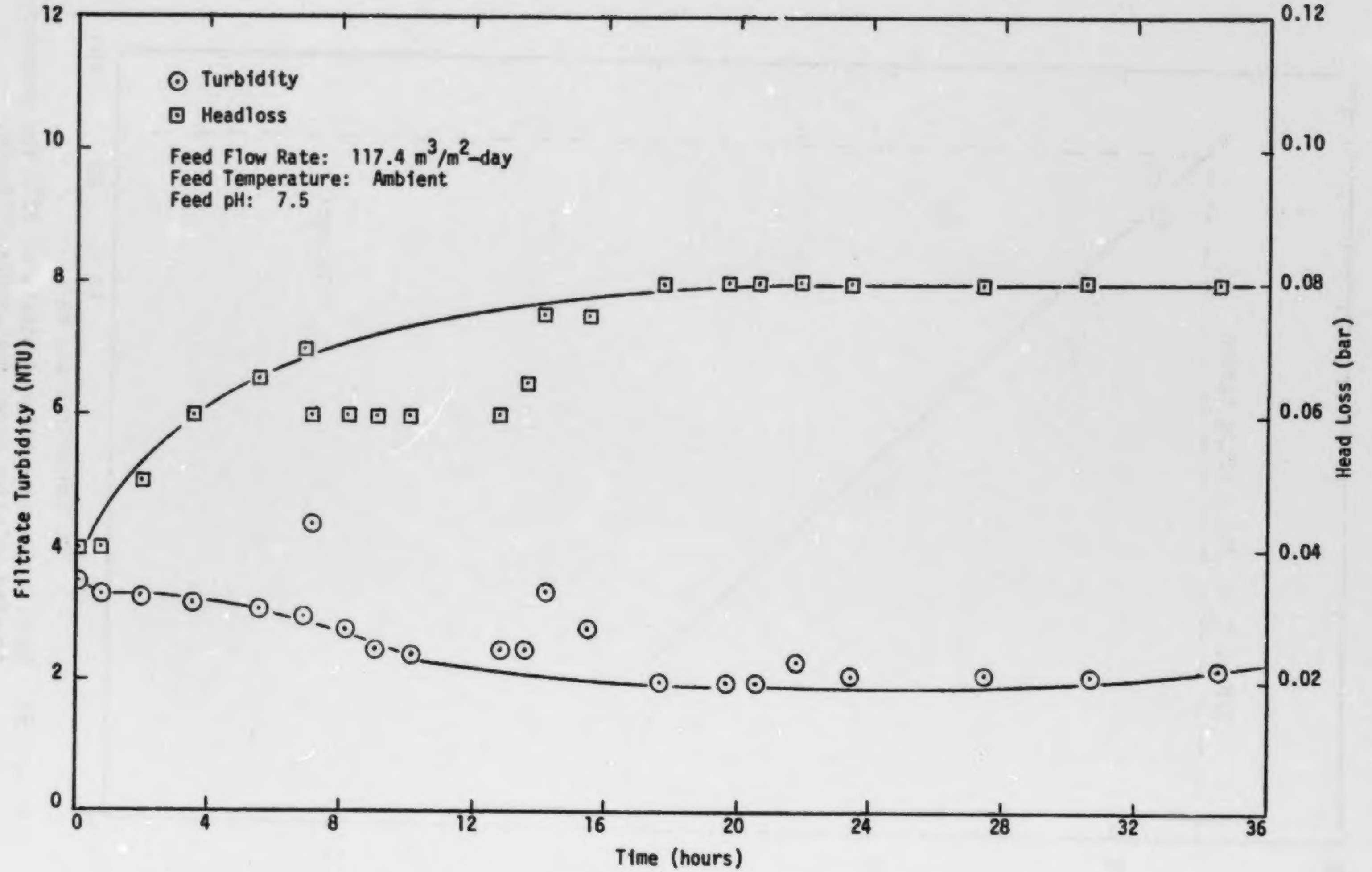

Figure 52. Filtrate turbidity and column head loss vs. time for dual-media depth filtration of secondary treated solution crumb wastewater; 0.05 m diameter column.

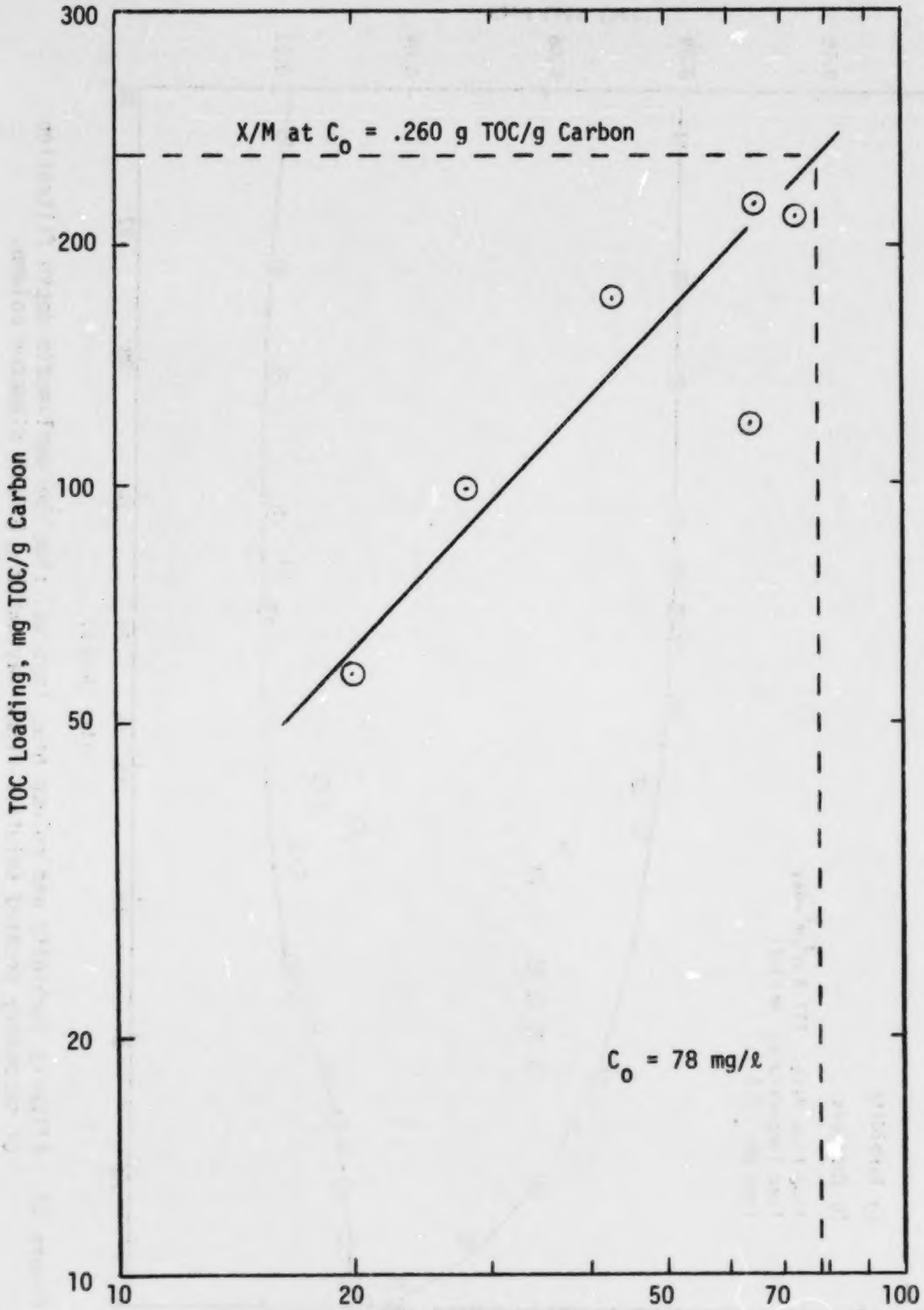

Figure 53. Equilibrium adsorption isotherm at 20°C for secondary treated solution crumb dual-media filtrate.

turbidity throughout the 35-hour run remained below 4 NTU and, for the most part, was less than 2.5 NTU. As observed in Figure 52, breakthrough did not occur. A filter service time of this duration exceeds normal practice indicating depth filtration of SSC wastewater is an economically viable unit process. The column headloss during the SSC processing remained below 0.55 bar (8 psig) and only minor surface straining was observed.

The filtrate turbidity vs. time plot for processing of the SSC wastewater through the 0.23 m diameter column is shown in Figure B5 of Appendix B. An average filtrate turbidity of 3 NTU was achieved. Column headloss was not measured during this run.

Backflush Requirements--The standard backflush operating conditions [backwash flow rate = 646-881 m^3/m^2-day (11-15 gpm/ft^2); duration = 6-8 minutes] were used to regenerate the columns. Neither column was fully loaded before backflushing. No difficulties were encountered in removing those solids which had accumulated.

Contaminant Removal--Feed, filtrate, and backwash-water analyses for dual-media depth filtration of the secondary solution crumb wastewater are presented in Table 44. As expected, the only parameters to show significant removals were suspended solids and turbidity. For the two depth filter runs, the filtrate averaged 6 mg/ℓ suspended solids with a turbidity of 2.6 NTU. A filtrate of this quality would be an acceptable feed to a carbon column operating in an upflow mode.

Carbon Adsorption--

The adsorption isotherm at 20°C for the SSC dual-media filtrate is presented in Figure 53. The slope of this isotherm (1.06) is moderate and indicates good adsorption of organics throughout a range of 20-80 mg/ℓ TOC.

The TOC breakthrough curves for carbon-column treatment of the SSC depth filter effluent are shown in Figure 54. The test was terminated before complete breakthrough occurred in the fourth column because of a pump failure. Sufficient data were obtained, however, to evaluate the economics of meeting the BATEA COD guideline. The curve for column 4 indicates a TOC of 40 mg/ℓ (i.e., COD of ~120 mg/ℓ) at 85 liters processed. Processing beyond this point would allow the effluent COD to exceed the BATEA standard of 130 mg/ℓ.

The required carbon dosage would be 0.61 kg/m^3 (5093 lbs/MM gal). This represents a carbon replacement cost of \$0.53/m^3 (\$2.00/1000 gal) processed. This replacement cost exceeds the entire operating and maintenance projection for depth filtration and carbon treatment of the SSC wastewater presented in the Development Document. The projected treatment costs (corrected to March, 1976, dollars) were \$0.23/m^3 (\$0.87/1000 gal) for the addition of sand filtration and carbon adsorption to the existing secondary treatment facility. Overall costs for SSC wastewater processing by primary and secondary treatment and dual-media filtration and activated carbon are presented in Section 7.

TABLE 44. CONTAMINANT ANALYSES FOR DUAL MEDIA DEPTH FILTRATION AND CARBON ADSORPTION OF SECONDARY TREATED SOLUTION CRUMB WASTEWATER

Contaminant	Feed As Received	pH Adjusted Feed	0.05m Diameter Column Backwash	0.23m Diameter Column Composite Filtrate	0.05m Diameter Column Composite Filtrate	Composite Carbon Effluent
Total Dissolved Solids (mg/l)	---	875	890	---	884	820
Suspended Solids (mg/l)	77	24	1010	5	7	<5*
Oil and Grease (mg/l)	7	7	14	---	<4	(9)
TOC (mg/l)	---	79	226	70	78	30
COD (mg/l)	239	256	299	---	237	72
BOD_5(mg/l)	65*	7*	170	---	30	4
Surfactants (mg/l)	---	0.41	---	---	---	0.05
Iron (mg/l)	---	1.0	15	---	<1	<1
Lead (mg/l)	---	<1	<1	---	<1	<1
Color (Units)	---	70	70	---	60	20
Turbidity (NTU)	14	16	285	3.0	2.1	2.5
pH	9.2	7.4	7.4	7.4	7.2	7.4
Conductivity (μmhos/cm)	1250	1400	1270	1350	1200	1350

*Sample stored at 4°C for six days before analyzing.

Note: ( ) Indicates suspected error in analysis.

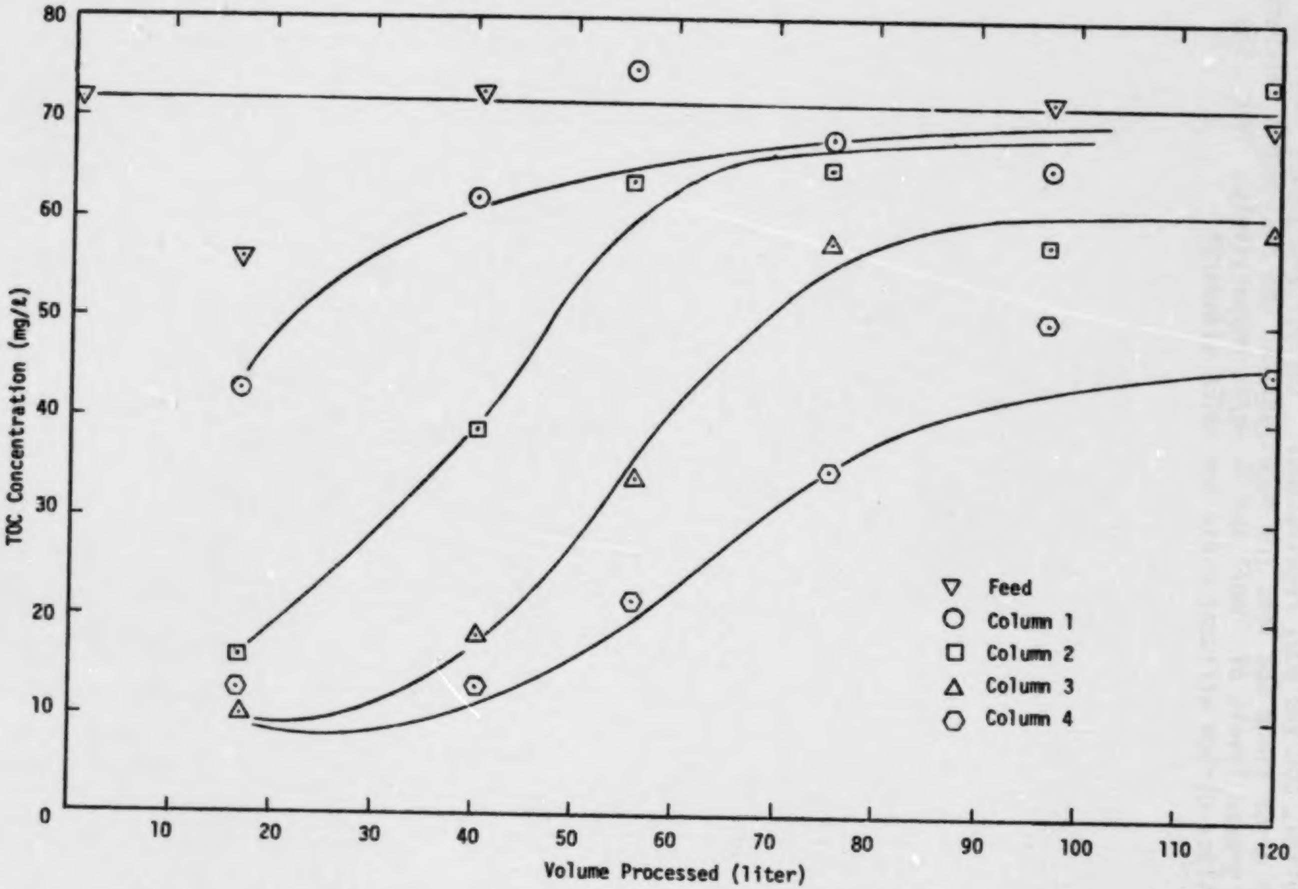

Figure 54. TOC breakthrough curves for carbon column treatment of secondary treated solution crumb dual-media filtrate.

Contaminant analyses for carbon treatment of the SSC wastewater are given in Table 44. The composite carbon effluent satisfies the BATEA suspended solids, COD and BOD_5 requirements. The oil and grease level of 9 mg/ℓ is in error since the feed (as received) and the dual-media filtrate had oil and grease levels of 7 mg/ℓ and <4 mg/ℓ, respectively. Thus, the SSC depth filter carbon effluent meets the BATEA standards.

SECTION 7

PREFERRED TREATMENT OPTIONS AND ASSOCIATED COSTS

INTRODUCTION

The preferred treatment options presented in this section are based on limited experimental data. With the exception of tests conducted with in-process latex manufacturing wastes, tests were conducted with only one sample of each waste type obtained from one manufacturing site. The breadth of applicability of these recommendations in the synthetic rubber industry is therefore uncertain at present and should be verified by on-site demonstration programs.

The economic analyses for the use of dual-media depth filtration and carbon adsorption were obtained from the Effluent Guidelines Development Document. The costs given in the Development Document were based on August, 1971, dollars. These costs were adjusted to March,1976, dollars by using the ratio of the Chemical Engineering plant cost indices for 1971 and March, 1976, as follows:

$$\text{August, 1971, dollars} \times \frac{\text{CE March, 1976, Index of 188.4}}{\text{CE 1971 Annual Index of 132.2}} = \text{March, 1976, dollars}$$

The capital and operating costs for ultrafiltration and reverse osmosis are also based on March, 1976, dollars. These costs are based on system estimates provided by Abcor, Inc.

Land costs were excluded from all total capital cost estimates, since they are dependent upon plant location (4). Smaller land area requirements are projected, however, when membrane separation systems are employed to reduce the loading on (or to replace) primary and secondary treatment operations. This may be a major consideration for plants operating in urban areas which have limited expansion land available.

System depreciation was not computed into the annual operating costs for any of the treatment options presented in this report. A short-term depreciation period of 5 years (straight line) is currently acceptable under Internal Revenue Service Regulations pertaining to industrial pollution control equipment (4).

LATEX MANUFACTURING WASTEWATER

Preferred Treatment

Two modifications to the present waste stream flow pattern are proposed for latex producing plants. These changes (dashed lines), along with the present wastewater flow pattern (solid lines), are shown schematically in Figure 55. The concentration of the LWW stream for recovery of latex involves two steps: reuse of rinse waters to build up their latex concentration to a 0.5% solids level and ultrafiltration of the 0.5% latex stream to a 15% solids (30X) concentration. The benefits of this treatment scheme include:

- Reduction of overall waste stream flow from 13.3 m^3/metric ton (1600 gal/1000 lb) product to 5.4 m^3/metric ton (650 gal/1000 lb) product.
- Reduction of the raw waste stream COD loading from 37 kg/metric ton (lb/1000 lb) product to 3.1 kg/metric ton (lb/1000 lb) product.
- Recovery of 0.09 m^3 (24 gal) of 15% latex solids/metric ton product @ $0.11 per kg of latex (dry weight basis) resulting in a credit of $7.52/metric ton ($3.42/1000 lb) product.

It is of interest to compare the anticipated COD concentration of the remaining end-of-pipe waste for the scheme of Figure 55 to the BPCTCA and BATEA guideline concentrations:

Assay	Present Raw Waste Loading	Predicted Raw Waste Loading Following Ultrafiltration of LWW Stream	BPCTCA Guidelines	BATEA Guidelines
COD (kg/ metric ton)	30-40	2-4	6.85	1.78

The significant reduction in COD loading (~90%) means that the BPCTCA effluent guideline for COD could be met without any further treatment of the total wastewater flow. Effluent suspended solids, BOD_5, and oil and grease levels after incorporation of in-process ultrafiltration are difficult to predict due to the limited data available. It is clear, however, that virtually no suspended solids will be present in the ultrafiltrate discharge and that sizable BOD_5 reductions will occur. It is predicted that the BATEA COD guideline would be easily achieved by primary and secondary treatment of the ultrafiltrate.

The data obtained from the combined ultrafiltration/reverse osmosis treatment experiment (see page 64) indicate that closed loop operation on tank and tank car washdown wastewaters is feasible. Therefore, reverse osmosis treatment of the ultrafiltrate should be considered in lieu of conventional treatment processes if the plant is located in an urban area

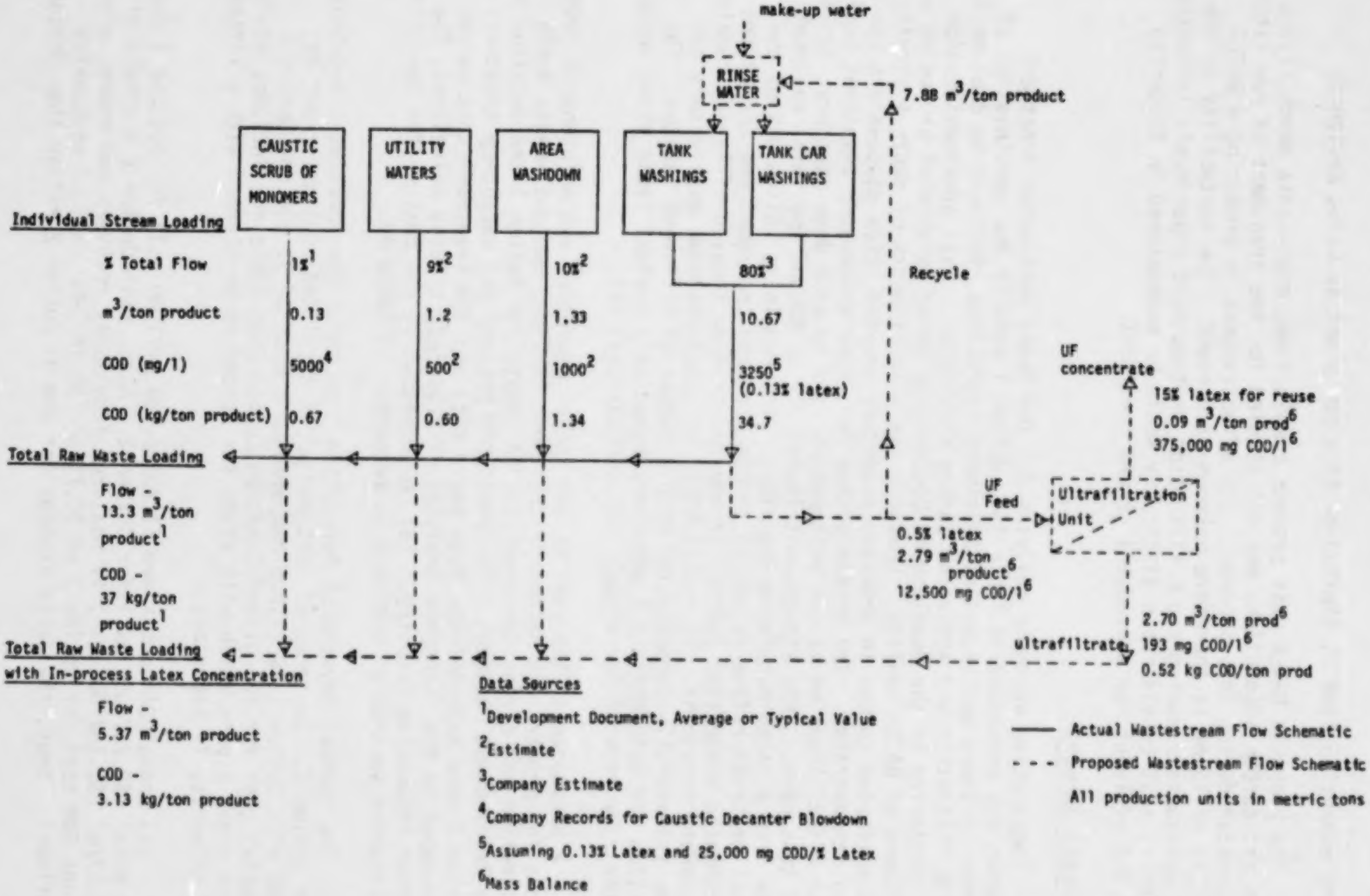

Figure 55. Actual and proposed waste stream flow patterns for latex wastewater.

where expansion land is limited or if a new plant is being designed.

The proposed BATEA unit process combination, dual-media depth filtration and carbon adsorption, was not studied for the treatment of raw latex wastewater during this program. Its effectiveness in producing a BATEA quality effluent is therefore unknown at present. The instability of the RLX wastewaters during depth filtration pretreatment experiments indicates, however, that considerable difficulty would be encountered in filtering the RLX effluent for subsequent carbon treatment.

Economic Summary

Comparative economic analyses for two latex wastewater treatment schemes are presented in Table 45. Option 1 entails the continuation of current primary and secondary treatment operations, followed by dual-media depth filtration and activated carbon adsorption. This treatment option was projected in the Development Document as being capable of producing an effluent of BATEA quality. However, the effectiveness of depth filtration and activated carbon in treating secondary treated latex wastewaters has not been demonstrated. The second option for latex wastewater treatment begins with ultrafiltration of the wastewaters used to wash down reactors, tanks, and tank cars. This stream contributes 70% to 90% of the total wastewater flow from a latex manufacturing plant. The remaining 10% to 30% of the total wastewater flow is passed through primary treatment and the entire pretreated wastewater (ultrafiltrate and primary treated effluent) receives secondary treatment. Ultrafiltration of latex washdown wastewaters has been successfully demonstrated with a number of different latices. The costing for both Options 1 and 2 are based on a typical latex plant wastewater flow rate of 382 m^3/day (101,000 gal/day) (4).

A breakdown of the capital and annual operating and maintenance (O&M) costs for primary and secondary treatment (BPCTCA) and dual-media depth filtration and carbon treatment (BATEA) costs for Option 1 are detailed in the Development Document. The costs for primary and secondary treatment in Option 2 were extrapolated from these data and the treatment cost curves developed in the "Economic Analysis of Proposed Effluent Guidelines, The Rubber Processing Industry." (3) A breakdown of the costing for the ultrafiltration section of Option 2 is presented in Table 46.

The capital investment for Option 1 is twice the investment required for Option 2. In terms of cost per m^3 of total influent water per day (382 m^3), Option 1 is $2,925 compared to a cost of $1,504 for Option 2. The capital cost for the ultrafiltration system (see Table 46) includes stainless steel piping which will allow the system to be cleaned with a variety of solvents, if necessary.

The annual O&M costs are $1.23/$m^3$ ($4.64/1000 gal) for Options 1 and $0.68/$m^3$ ($2.28/1000 gal) for Option 2. Also, with Option 2 a credit of $0.57/$m^3$ ($2.14/1000 gal) is realized from latex recovery and reuse, giving a net O&M cost for Option 2 of $0.11/$m^3$ ($0.14/1000 gal) of wastewater influent. Thus, the daily savings for use of Option 2 rather than Option 1

TABLE 45. ECONOMIC ANALYSIS OF TREATMENT OPTIONS FOR LATEX WASTEWATERS (MARCH, 1976 DOLLARS)

Option I.	Current Treatment and Development Documents' Projected Advanced Treatment	Capital Costs, $	Annual Operating and Maintenance Costs, $	Annual Credits, $
	Primary and secondary treatment of total plant effluent (4)	907,725	85,000	---
	Dual-media filtration and activated carbon treatment of total plant effluent (effectiveness of treatment in question)(4)	209,475	85,000	---
		1,117,200	171,000	---
	Cost per m^3 of total influent per day, $	2,920	---	---
	Cost per m^3 influent, $	---	1.23	---
Option II.	Proposed Treatment			
	Ultrafiltration of latex washdown waters	157,500	45,780	78,891
	Primary treatment of 20% of total effluent(4)	136,780	8,550	---
	Secondary treatment of ultrafiltrate and primary treated effluent (reduced flow and loading - assume 1/3 of cost for secondary treatment given in Reference (4))	280,197	39,900	---
		574,477	94,230	78,891
	Cost per m^3 total influent per day, $	1,504	---	---
	Cost per m^3 influent, $	---	0.68	0.57
	Daily savings of proposed treatment over Option I treatment, $428.			
	Typical plant flowrate - 382 m^3/day			

TABLE 46. BREAKDOWN OF CAPITAL COSTS AND ANNUAL OPERATING COSTS FOR ULTRAFILTRATION SYSTEM TREATING LATEX WASTEWATERS (TABLE 45, OPTION II)

A. CAPITAL COST

87,500		Estimated UF System Cost; 47 m^2 membrane area, 304 S.S. piping based on projected design flux of 1.64 m^3/m^2-day
43,750		Field Installation, Estimated at 50% of UF System Cost
	131,250	
26,250	26,250	Auxiliary Tanks, Pumps, Piping - estimated at 20% of UF installation cost
	157,500	Total installed cost

B. ANNUAL OPERATING COST

7,850	Pumping power, 22.5 kWh (30 hp), 365 days, 24 hrs/day @ \$0.04/kWh
15,330	O + M Labor, 4 hrs/day over 3 shifts @ \$6/hr + 75% Fringe and Overhead
6,390	Supervisory Labor, 1 hr/day over 3 shifts @ \$10/hr + 75% Fringe and Overhead
3,500	Maintenance Materials - estimated @ 4% UF System Cost
4,420	Cleaning Chemicals - 2 detergent cleanings per week
2,890	Taxes and Insurance - assumed @ 2% of Total Installed Cost
5,400	Membrane Replacement - 2 yr life
45,780	

are $428 ($156,000/year).

Based on the experimental results of this program and the above economic analysis, concentration and recovery by ultrafiltration of within-process latex washdown wastewaters is recommended. Conventional primary and secondary treatment is recommended for the remaining end-of-pipe latex wastewater, and secondary treatment is recommended for the ultrafiltrate. Advanced treatment of the secondary effluent is not believed to be necessary to meet BATEA guidelines and is not recommended. Reverse osmosis treatment of the ultrafiltrate for closed-loop recycle of washdown wastewaters is technically feasible and may be economically attractive in certain special cases.

EMULSION CRUMB MANUFACTURING WASTEWATER

Preferred Treatment

Continued use of primary and secondary treatment for processing of end-of-pipe emulsion crumb wastewaters is recommended. None of the alternative treatment options investigated appear suitable for processing the REC wastewater because of its high concentrations of dissolved solids and TOC. In-process ultrafiltration of reactor washdown wastewaters, to lower the COD loading on the secondary treatment operation, is not feasible because of the infrequent flow and non-uniform nature of the washdown wastewaters. These washdown wastewaters differ from those generated in latex plants and are not amenable to concentration by ultrafiltration.

The use of dual-media depth filtration and carbon adsorption for the treatment of emulsion crumb secondary effluent appears to be the most practical approach to meeting BATEA standards. The effluent from the secondary treatment system presently meets or approaches the BPCTCA standards. Dual-media depth filtration of the SEC wastewater to lower the suspended solids loading followed by activated carbon treatment for organics reduction would produce an effluent of BATEA quality. In emulsion crumb plants, the backwash waters from the depth filters and carbon columns would be returned to the secondary treatment operation while the spent carbon would be regenerated on-site (4).

Economic Summary

An economic analysis of the recommended treatment for emulsion crumb wastewaters is presented in Table 47. This recommendation is identical to the Development Document's projected BATEA treatment of primary and secondary treatment followed by DMDF and carbon treatment. A detailed cost analysis for these unit processes is found in Reference (4). The data presented in Table 47 are based on a typical emulsion crumb rubber plant wastewater flow rate of 5,614 m^3/day (1,483,000 gal/day)(4).

The capital expenditure for the entire treatment system is $760/$m^3$

TABLE 47. ECONOMIC ANALYSIS OF PROPOSED TREATMENT OPTIONS FOR EMULSION CRUMB WASTEWATERS (MARCH, 1976 DOLLARS)

Current Treatment and Development Documents' Projected Advanced Treatment	Captial Costs, $	Annual Cperating and Maintenance Costs,$
Primary and secondary treatment of total plant effluent (4)	2,852,850	356,250
Dual-media filtration and activated carbon treatment of total plant effluent (4)	1,412,175	249,375
	4,265,025	605,625
Cost per m^3 of total influent per day, $	760	---
Cost per m^3 influent, $	---	0.30
Typical plant flowrate - 5,614 m^3/day		

($2.88/gal) of total influent per day. 67% of this amount has already been invested at most sites for primary and secondary treatment facilities. The net investment required to reach BATEA standards is therefore estimated at 1.5 million dollars for the "typical" plant. The major portion of the operating and maintenance costs are also associated with current treatment processes. Incorporation of dual-media depth filtration and activated carbon treatment is expected to raise the O&M costs by $0.12/m³ ($0.46/1000 gal) to $0.30/m³ ($1.12/1000 gal). These cost figures were not verified during this program since carbon column breakthrough was not obtained. Further testing is essential to develop an accurate economic profile of DMDF/ACA treatment of emulsion crumb wastewaters.

SOLUTION CRUMB MANUFACTURING WASTEWATER

Preferred Treatment

For solution polymerization, two alternative wastewater treatment schemes are recommended. First, for existing facilities which currently have primary and secondary treatment, the addition of dual-media depth filtration and carbon adsorption is preferred. Second, for existing facilities which do not have secondary treatment, and for new sources, treatment of the raw wastewater by ultrafiltration and reverse osmosis is recommended. Both methods of treating the solution crumb wastewater are effective and result in a high quality effluent as shown in Table 48.

TABLE 48. COMPARISON OF REVERSE OSMOSIS AND CARBON ADSORPTION PRODUCT WATERS WITH BATEA GUIDELINES FOR SOLUTION CRUMB MANUFACTURING WASTES

Assay	Reverse Osmosis Composite Permeate	Carbon Column Composite Effluent	BATEA Guidelines
Suspended Solids (mg/ℓ)	nil	< 5	10
Oil and Grease (mg/ℓ)	7*	9*	5
COD (mg/ℓ)	36	72	130
BOD_5 (mg/ℓ)	4	4	5
Dissolved Solids (mg/ℓ)	141	820	---
Color (units)	5	20	---

*Error suspected in analysis. Actual oil and grease level < 4 mg/ℓ.

The reverse osmosis product water is superior to the carbon effluent in all respects and, because of its low dissolved solids and color, is expected to be reusable within the plant for boiler and cooling tower makeup. It may also be suitable for the crumb slurrying operation.

The use of ultrafiltration and reverse osmosis treatment is not recommended for those existing facilities with secondary treatment presently in operation since addition of depth filtration and carbon adsorption is a more cost-effective alternative. If either upgrading or expansion of the secondary treatment process at an existing plant is contemplated, then the alternative of ultrafiltration/reverse osmosis should be considered.

Economic Summary

As stated above, two viable options are available for treatment of solution crumb wastewaters to meet BATEA standards. Option 1 is primary and secondary treatment of the raw wastewater followed by dual-media depth filtration and carbon treatment of the secondary effluent. A detailed economic analysis of this option is given in the Development Document; however, the operating costs given there for carbon replacement have been shown during this program to be quite low. These costs have been appropriately corrected in the ensuing presentation.

Option 2 consists of ultrafiltration of the raw wastewater followed by reverse osmosis of the ultrafiltrate. This option is divided into two segments to facilitate the presentation of the economics. Option 2A economics are based on the use of tubular ultrafiltration modules, while Option 2B economics were developed for more compact spiral-wound ultrafiltration modules.

All experimental work was performed with membranes in the tubular geometry; however, spiral-wound cartridges are potentially applicable for treatment of the RSC wastewater. The overall economic analysis for Options 1, 2A, and 2B is presented in Table 49. Breakdown of the capital and O&M costs for Option 2 are given in Table 50 for tubular ultrafiltration, in Table 51 for spiral-wound ultrafiltration, and in Table 52 for reverse osmosis. The economics of all options are based on a typical solution-crumb-plant daily flow rate of 1336 m^3/day (353,000 gal/day)(4).

The capital cost for spiral-wound ultrafiltration/reverse osmosis treatment of the raw wastewater is $647/$m^3$ ($2.45/gal) of the daily total influent. This is about 30% lower than the capital cost of tubular ultrafiltration/reverse osmosis treatment and ~50% lower than the capital cost for Option 1. The annual O&M costs are also lowest for the spiral-wound ultrafiltration/reverse osmosis treatment combination. The O&M costs for the various options are $0.91/$m^3$ ($3.46/1000 gal), $0.84/$m^3$ ($3.18/1000 gal), and $0.62/$m^3$ ($2.35/1000 gal) for Option 1, Option 2A, and Option 2B, respectively.

Two factors have been omitted from the Option 2 annual operating costs. These factors are ultrafiltration and reverse osmosis concentrate disposal costs and credits for reuse of reverse osmosis permeate. The impact of these two factors on the overall Option 2 operating costs requires further study of alternative concentrate disposal options (other than hauling) which is beyond the scope of this report.

TABLE 49. ECONOMIC ANALYSIS OF TREATMENT OPTIONS FOR SOLUTION CRUMB WASTEWATER (MARCH, 1976, DOLLARS)

		Capital Costs, $	Annual Operating and Maintenance costs, $
Option I.	Current Treatment and Development Documents' Projected Advanced Treatment		
	Primary and secondary treatment of total effluent	1,154,250	102,600
	Dual-media filtration and activated carbon treatment of total effluent (Reference 4 costs modified based on experimental data)	530,000	343,142
		1,684,350	445,742
	Cost per m^3 influent per day, $	1,260	---
	Cost per m^3 influent, $	---	0.91
Option II.	Proposed Treatment for New Sources*		
	A. Ultrafiltration of raw wastewater-tubular membrane modules	620,400	282,360
	Reverse osmosis of ultrafiltrate	577,500	127,760
		1,197,900	410,120
	Cost per m^3 influent per day, $	898	---
	Cost per m^3 influent, $	---	0.84
	B. Ultrafiltration of raw wastewater, spiral wound membrane modules	288,700	176,670
	Reverse osmosis of ultrafiltrate	577,500	127,760
		866,200	304,430
	Cost per m^3 influent per day, $	647	---
	Cost per influent, $	---	0.62
	Typical plant flowrate-1336 m^3/day		

*Note: Concentrate disposal costs and reverse osmosis permeate reuse credits are not included.

TABLE 50. BREAKDOWN OF CAPITAL COSTS AND ANNUAL OPERATING COSTS FOR TUBULAR ULTRAFILTRATION SYSTEM TREATING SOLUTION CRUMB WASTEWATERS (TABLE 49, OPTION IIA)

A. CAPITAL COST

376,000		Estimated UF System Cost 820 m^3 membrane area, carbon steel and PVC piping, based on projected design flux of 1.64 m^3/m^2-day
188,000		Field Installation, 50% of UF System Cost
	564,000	
56,400	56,400	Auxiliary Tanks, Pumps, Piping - 10% of UF installation cost
	620,400	Total installed cost

B. ANNUAL OPERATING COST

117,730	Pumping power 336 kWh (450 hp), 365 days, 24 hrs/day @ $0.04/kWh
15,330	0 + M Labor, 4 hrs/day over 3 shifts @ $6/hr + 75% Fringe
6,390	Supervisory Labor, 1 hr/day over 3 shifts @ $10/hr + 75% Fringe
22,560	Maintenance Materials - estimated at 4% UF System Cost
17,680	Cleaning Chemicals - 2 detergent cleanings per week
12,400	Taxes and Insurance - assumed @ 2% of Total Installed Cost
90,270	Membrane Replacement - 2 yr life
282,360	

TABLE 51. BREAKDOWN OF CAPITAL COSTS AND ANNUAL OPERATING COSTS FOR SPIRAL-WOUND ULTRAFILTRATION SYSTEM TREATING SOLUTION CRUMB WASTEWATERS (TABLE 49, OPTION IIB)

A. CAPITAL COST

175,000		UF System Cost m^3 membrane area, carbon steel and PVC piping, based on projected design flux of 1.64 m^3/m^2-day
87,000		Field Installation, 50% of UF System Cost
	262,500	
26,200	26,200	Auxiliary Tanks, Pumps, Piping-10% of UF installation cost
	288,700	Total installed cost

B. ANNUAL OPERATING COST

78,490	Pumping power 224 kWh (300 hp), 365 days, 24 hrs/day @ $0.04 kWh
15,330	O + M Labor, 4 hrs/day over 3 shifts @ $6/hr + 75% Fringe
6,390	Supervisory Labor, 1 hr/day over 3 shifts @ $10/hr +75% Fringe
10,500	Maintenance Materials - estimated at 4% UF System Cost
17,680	Cleaning Chemicals - 2 detergent cleanings per week
15,780	Taxes and Insurance - assumed @ 2% of Total Installed Cost
32,500	Membrane Replacement - 2 yr life
176,670	

TABLE 52. BREAKDOWN OF CAPITAL COSTS AND ANNUAL OPERATING COSTS FOR REVERSE OSMOSIS SYSTEM TREATING SOLUTION CRUMB WASTEWATERS (TABLE 49, OPTION II)

A. CAPITAL COST

350,000		RO System Cost; 35 0.2m diameter permeates, carbon steel and PVC piping
175,000		Field Installation, 50% of RO System Cost
	525,000	
52,500	52,500	Auxiliary Tanks, Pumps, Piping - 10% of RO installation cost
	577,500	Total installed cost

B. ANNUAL OPERATING COST

39,250	Pumping power 112 kWh (150 hp), 365 days, 24 hrs/day @ $0.04/kWh
15,330	0 + M Labor, 4 hrs/day over 3 shifts @ $6/hr + 75% Fringe
6,390	Supervisory Labor, 1 hr/day over 3 shifts @ $10/hr + 75% Fringe
14,000	Maintenance Materials - estimated @ 4% RO System Cost
11,550	Taxes and Insurance - assumed @ 2% of Total Installed Cost
41,240	Membrane Replacement - 3 yr life
127,760	

At present, the most cost effective treatment plan would be dual-media filtration/carbon adsorption at plants with existing secondary treatment and spiral-wound ultrafiltration/reverse osmosis treatment at new facilities. Both treatment schemes are capable of producing a final effluent of BATEA quality.

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APPENDIX A

TABLE A-1. TOTAL ORGANIC CARBON (TOC) CONCENTRATIONS IN FEED AND ULTRAFILTRATE STREAMS FOR PRELIMINARY TOTAL RECYCLE TESTS WITH END-OF-PIPE CRUMB WASTEWATER

		TOC (mg/liter)			
			Ultrafiltrate		
Test Number	Feed Description/ Process Time	Feed	HFA	HFD	HFM
1	Raw Feed, 2 hours	278	225	200	183
	Raw Feed, 24 hours	266	201	198	189
	Raw Feed, 72 hours	253	167	151	136
2	Raw Feed - 1% Triton X-100, 1 hour	712	498	466	540
	Raw Feed - 1% Triton X-100, 24 hours	568	520	336	240
	Raw Feed - 1% Triton X-100, 40 hours	668	546	421	375

TABLE A-2. TOTAL ORGANIC CARBON (TOC) CONCENTRATIONS IN REVERSE OSMOSIS FEED AND PERMEATE STREAMS FOR PRELIMINARY TOTAL RECYCLE TESTS WITH END-OF-PIPE EMULSION ULTRAFILTRATION

Test Number	Process Time	TOC (mg/liter)			
			Permeate		
		Feed	CA	B-9	B-10
1	1 hour	178	14	15	-
	9 hours	176	12	13	-
2	1 hour	186	16	-	6
	12 hours	164	12	-	6

TABLE A-3. HISTORY OF SALT REJECTIONS FOR REVERSE OSMOSIS MODULES DURING PROCESSING OF SECONDARY TREATED EMULSION CRUMB DEPTH FILTER EFFLUENT

Module	Cumulative Operating Time (hrs)	Feed Concentration naCl/ (ppm)	Temperature (°C)	Permeate Flowrate m³/day	Feed Flowrate m³/day	Conversion %	Rejection %	Intrinsic Rejection	Remarks
Roga 4160 HR Spiral-Wound Cellulose Acetate (CA)	102	4450	27	3.8	27.7	13.6	93.6	0.940	Following raw emulsion crumb ultrafiltrate processing; 24 November 1975
		5700	26	3.8	31.3	12.2	91.8	0.922	Just prior to secondary treated emulsion crumb DMDF Filtrate processing; 13 January 1976
	162	5500	26	3.8	28.1	13.6	91.5	0.917	1X total recycle with B-10
	165	5000	26	3.8	28.7	13.1	92.0	0.925	Following secondary processing period Sec. Treated Emulsion Crumb DMDF Filtrate 1X-4.2X pumpdown
	209	6600	25	3.3	28.2	1.8	91.4	0.917	2X total recycle with B-10
	226	7250	25	2.9	28.5	10.3	91.7	0.918	4X total recycle with B-10
	-	4700	27	3.9	28.7	13.4	93.0	0.933	Following citric acid cleaning
duPont B-10 Hollow-Fine-Fiber Polyamide	104	5100	27	6.5	23.9	27.1	99.7	0.997	Following raw emulsion crumb ultrafiltrate processing; 24 November 1975, inlet pressure 38 bar.
	-	5800	25	9.8	28.6	34.3	99.3	0.994	Just prior to secondary treated emulsion crumb DMDF Filtrate processing; 13 January 1976, 55.2 bar
	109	7000	25	6.8	28.3	24.0	99.7	0.997	Following first batch concentration, 1X-4.2X pumpdown, 55.2 bar
	169	6290	26	4.9	24.2	20.2	99.4	0.995	1X total recycle with CA*
	172	5700	26	5.3	25.0	21.4	99.3	0.994	Following second pumpdown with CA*
	216	6170	25	4.4	24.9	17.5	99.1	0.992	2X total recycle with CA*
	233	8020	24	3.4	25.5	13.5	99.3	0.993	4X total recycle with CA*
	-	6350	27	7.6	21.0	30.8	99.6	0.997	Following citric acid cleaning and PT-8 treatment*

*Inlet pressure to B-10 between 38 bar and 36.57 bar when operated in series with CA module.

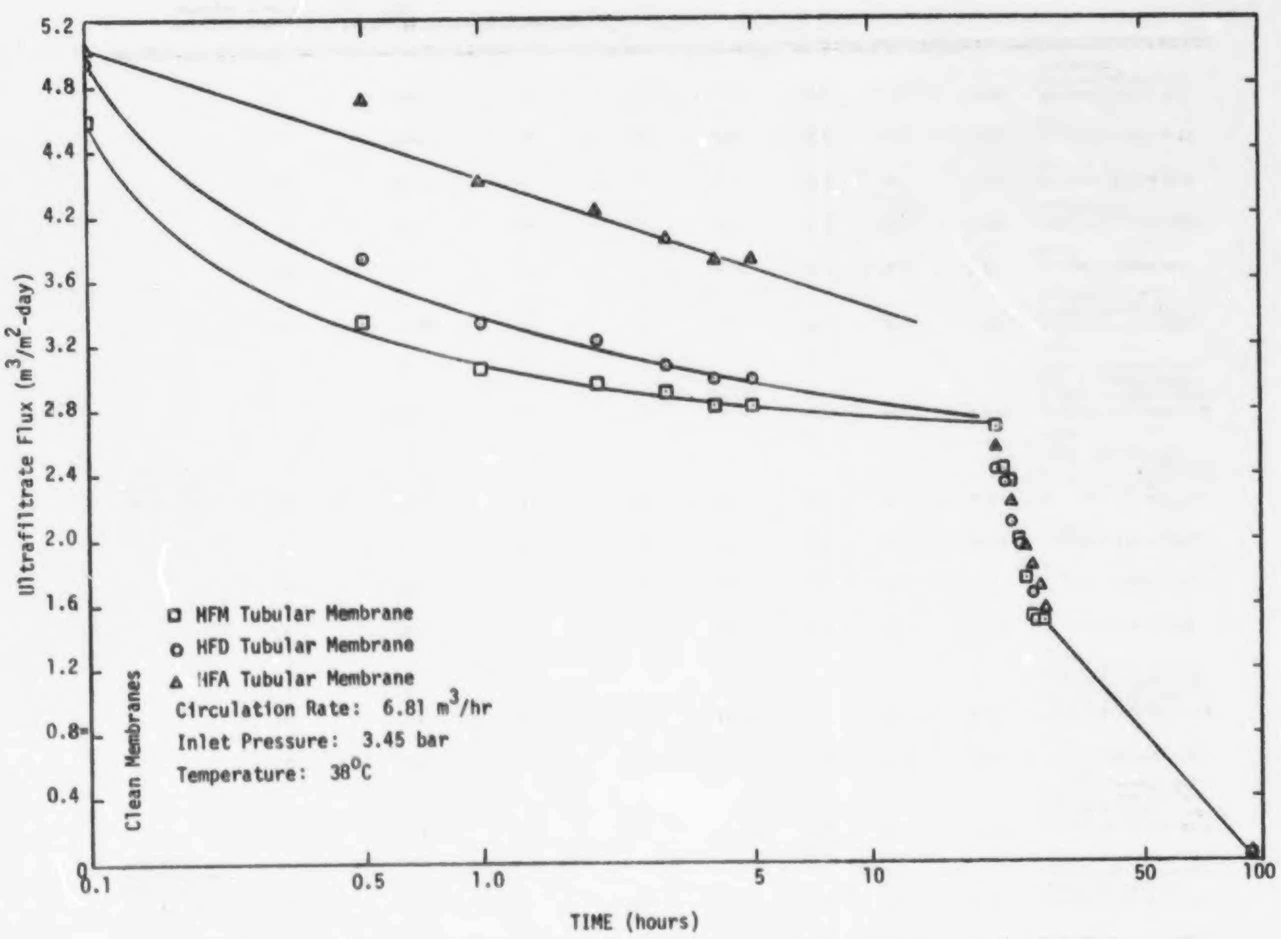

Figure A-1. Ultrafiltration membrane flux vs. time for 1X feed concentration of end-of-pipe emulsion crumb wastewater.

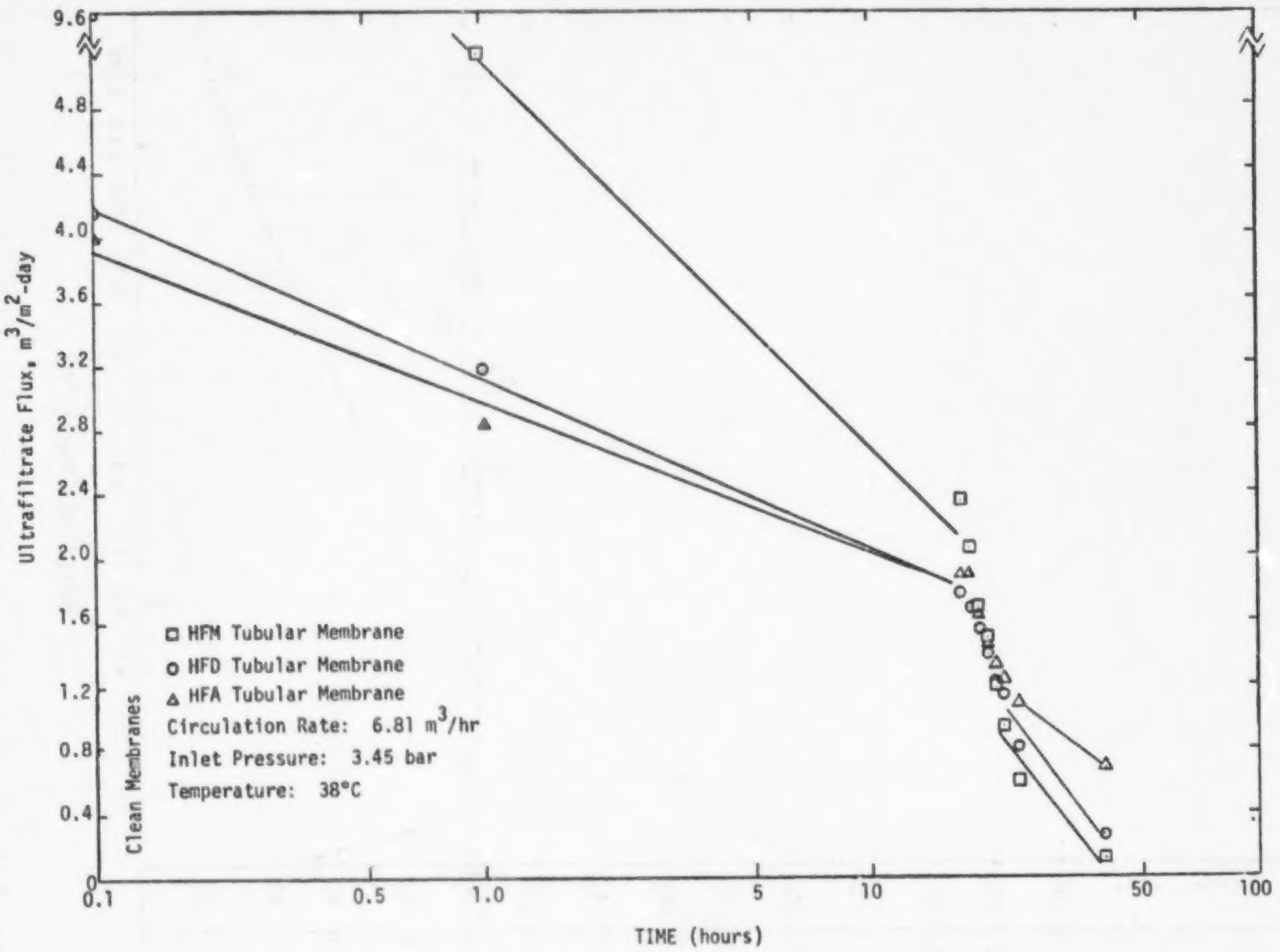

Figure A-2. Ultrafiltration membrane flux vs. time for 1X feed concentration of end-of-pipe emulsion crumb wastewater with 1% Triton X-100.

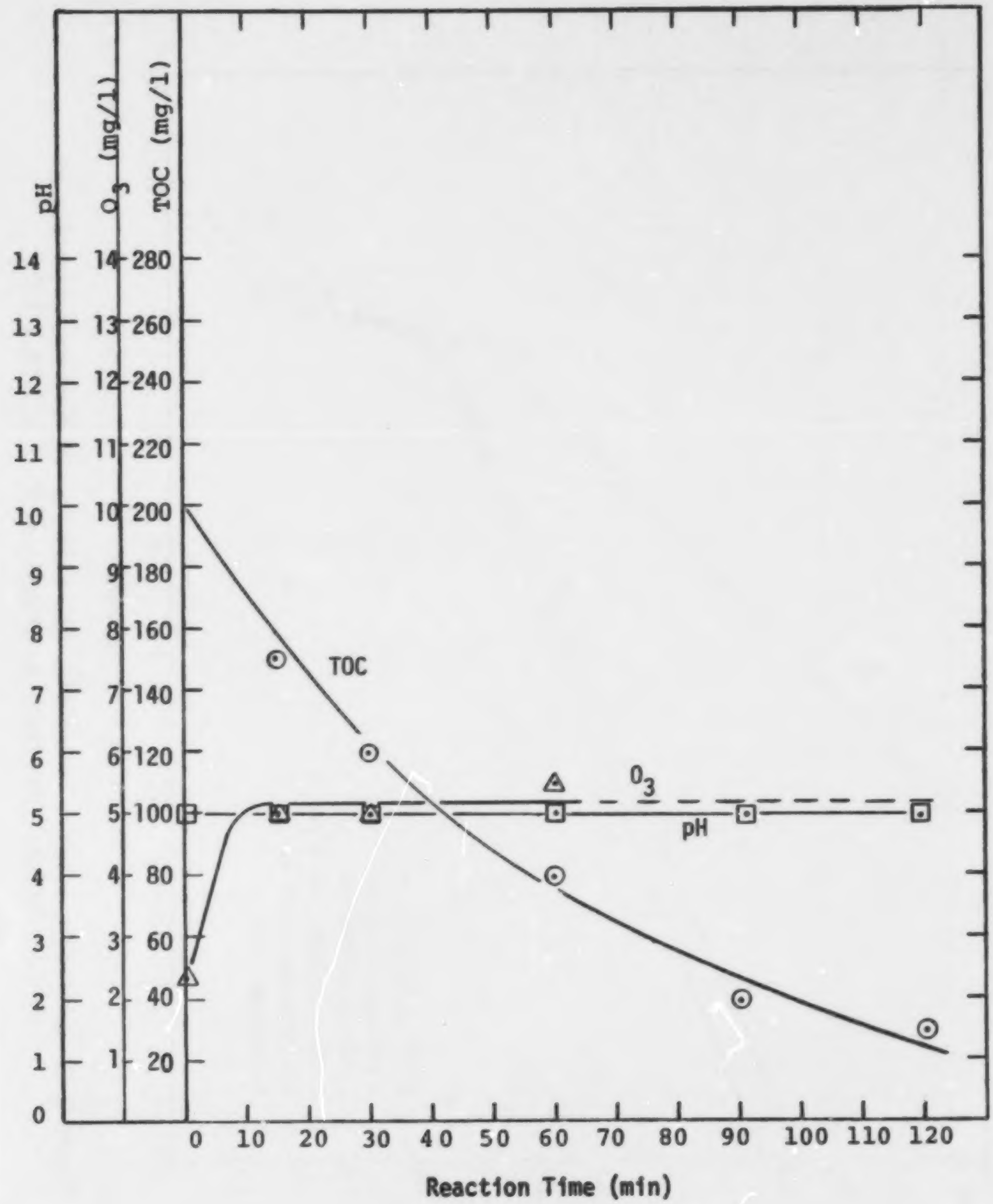

Figure A-3. Ozonation of end-of-pipe emulsion crumb ultrafiltrate at 30°C and pH 5 without UV light.

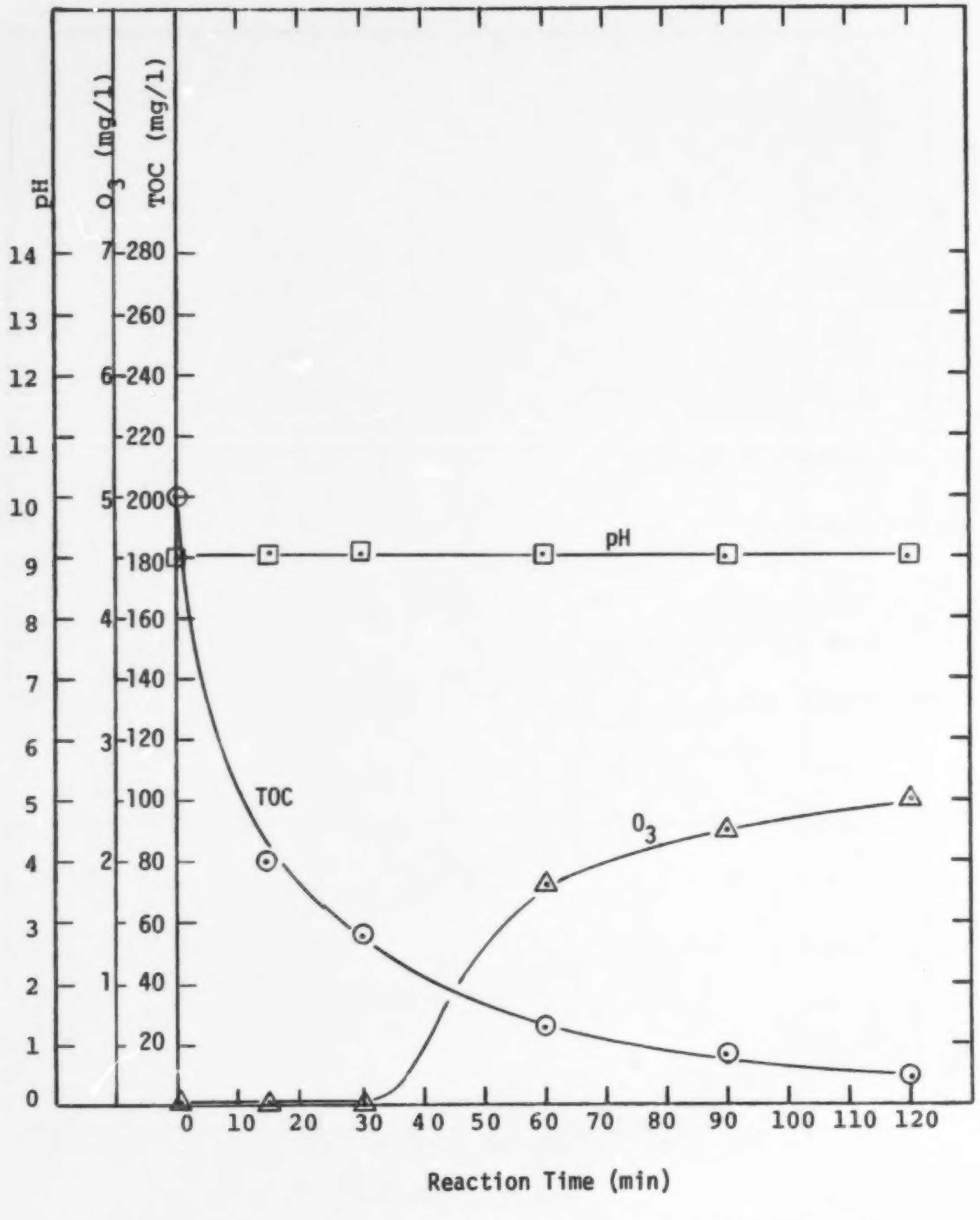

Figure A-4. Ozonation of end-of-pipe emulsion crumb ultrafiltrate at 30°C and pH 9 without UV light.

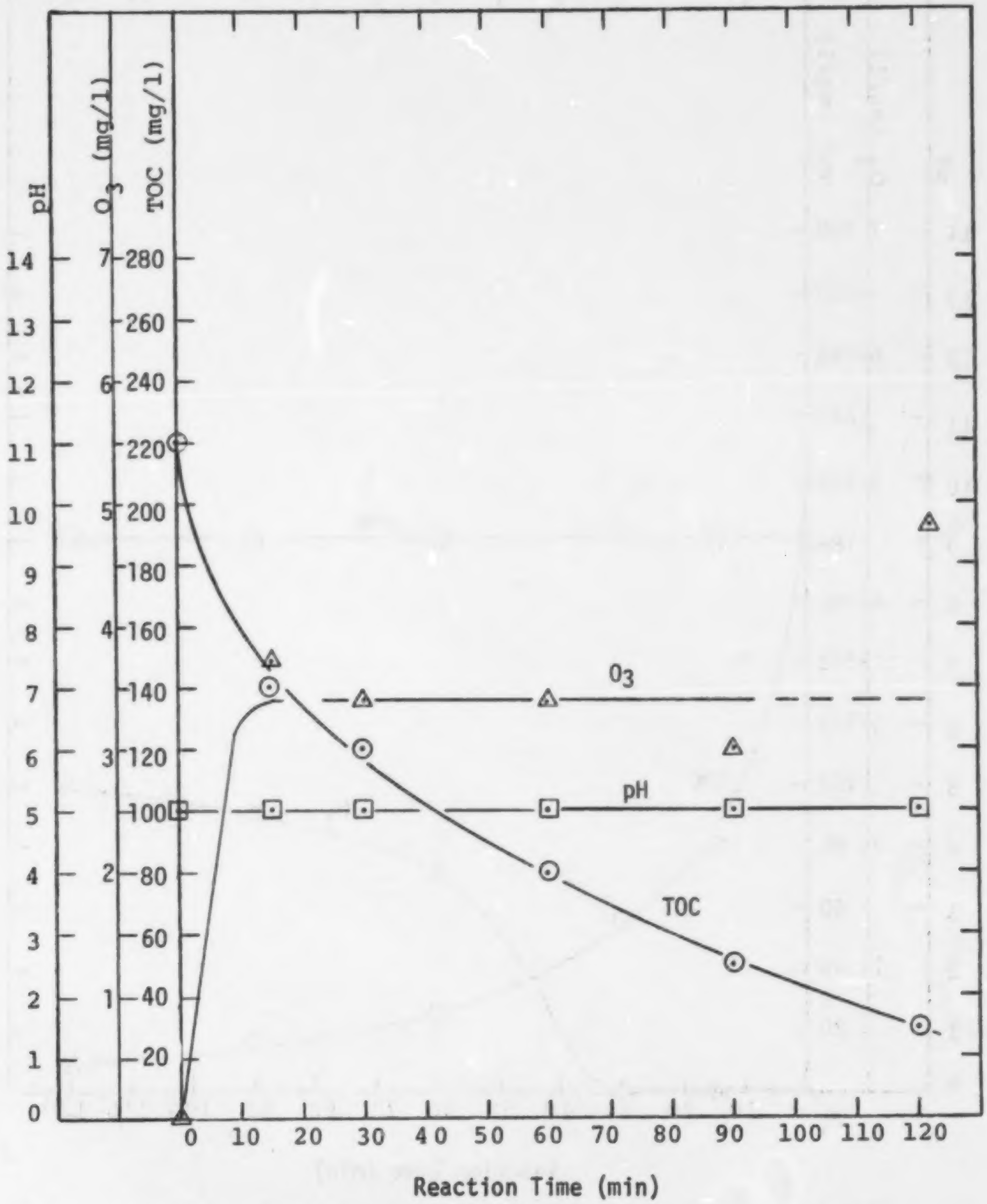

Figure A-5. Ozonation of end-of-pipe emulsion crumb ultrafiltrate at 30°C and pH 5 with UV light.

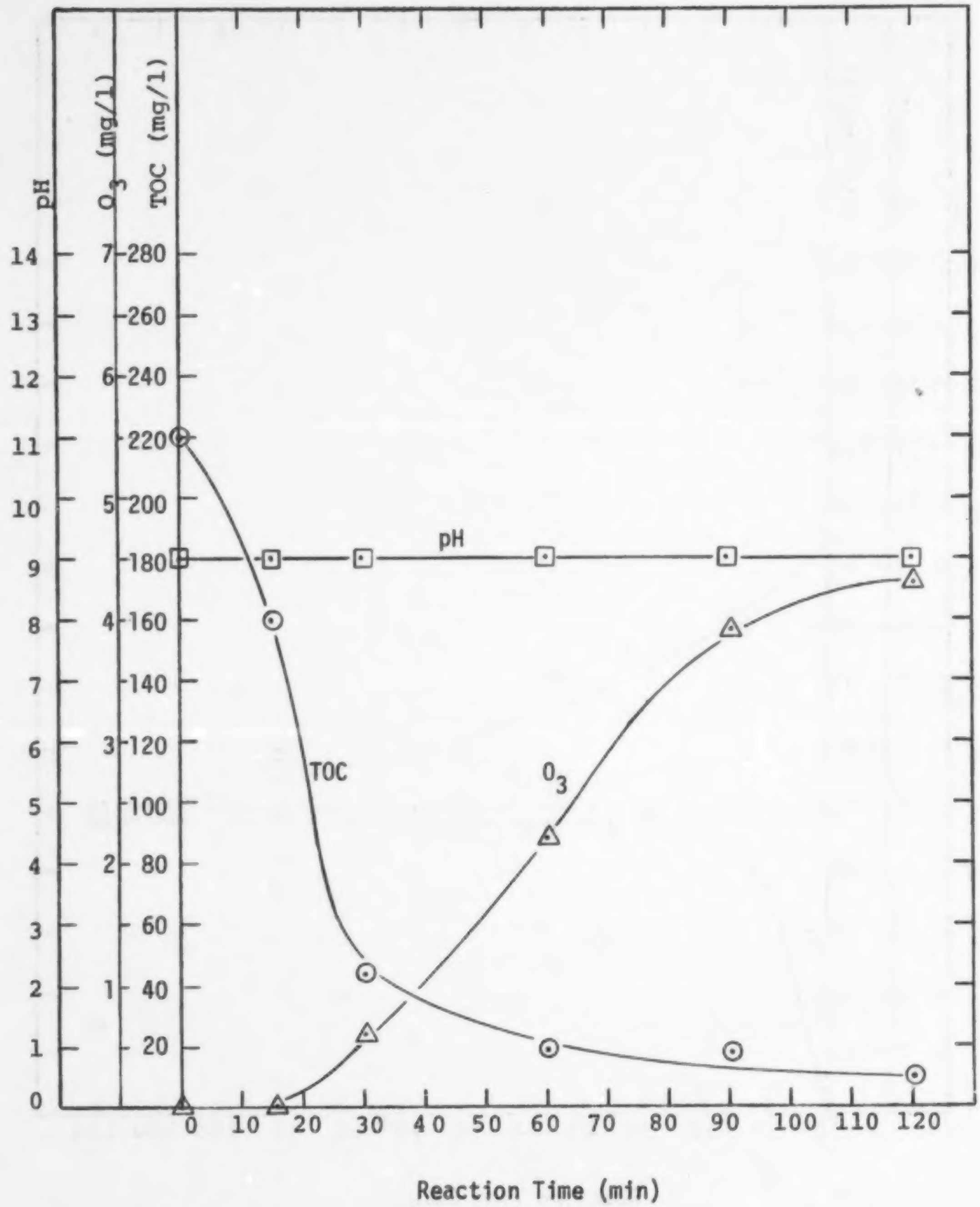

Figure A-6. Ozonation of end-of-pipe emulsion crumb ultrafiltrate at 30°C and pH 9 with UV light.

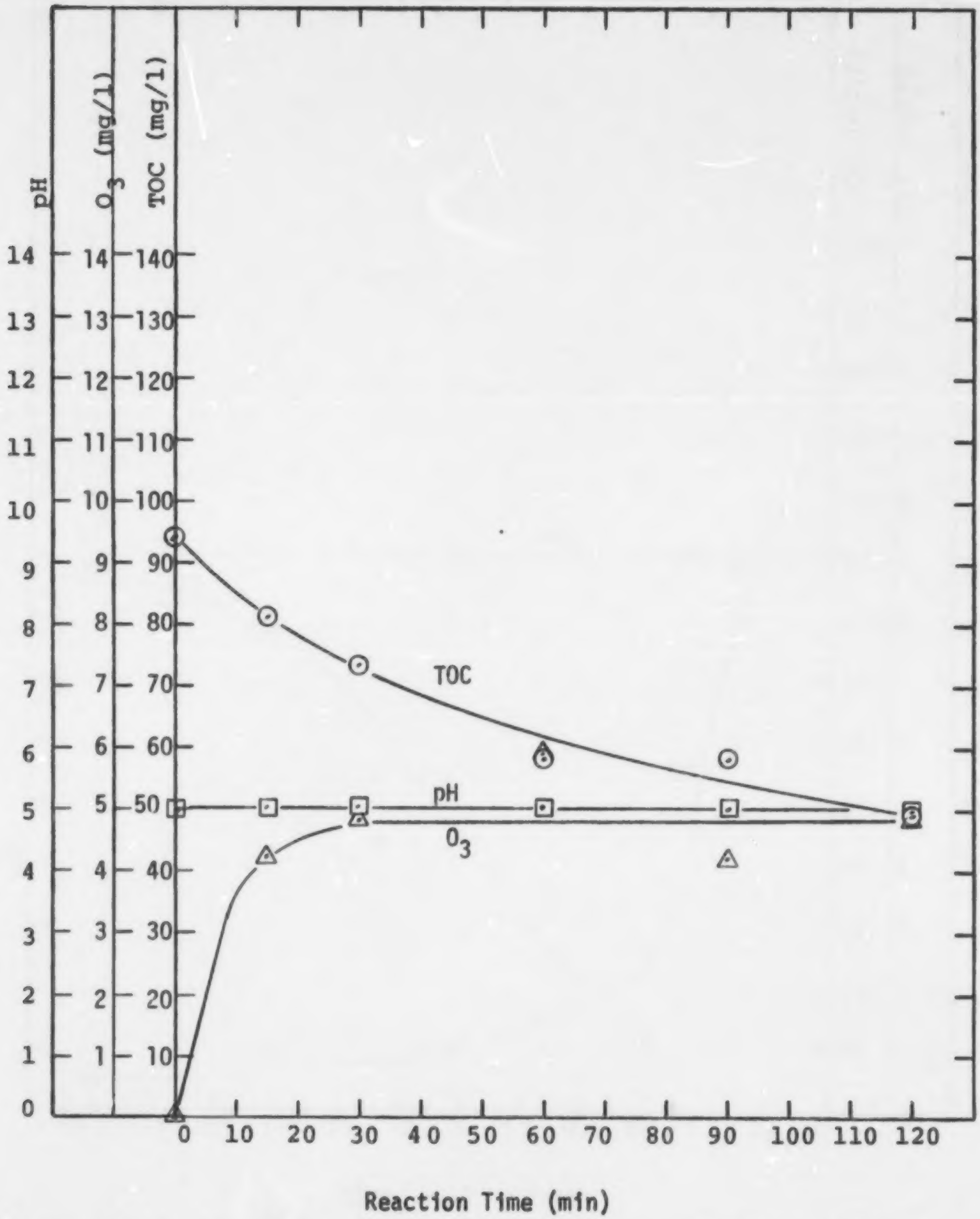

Figure A-7. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 5 without UV light.

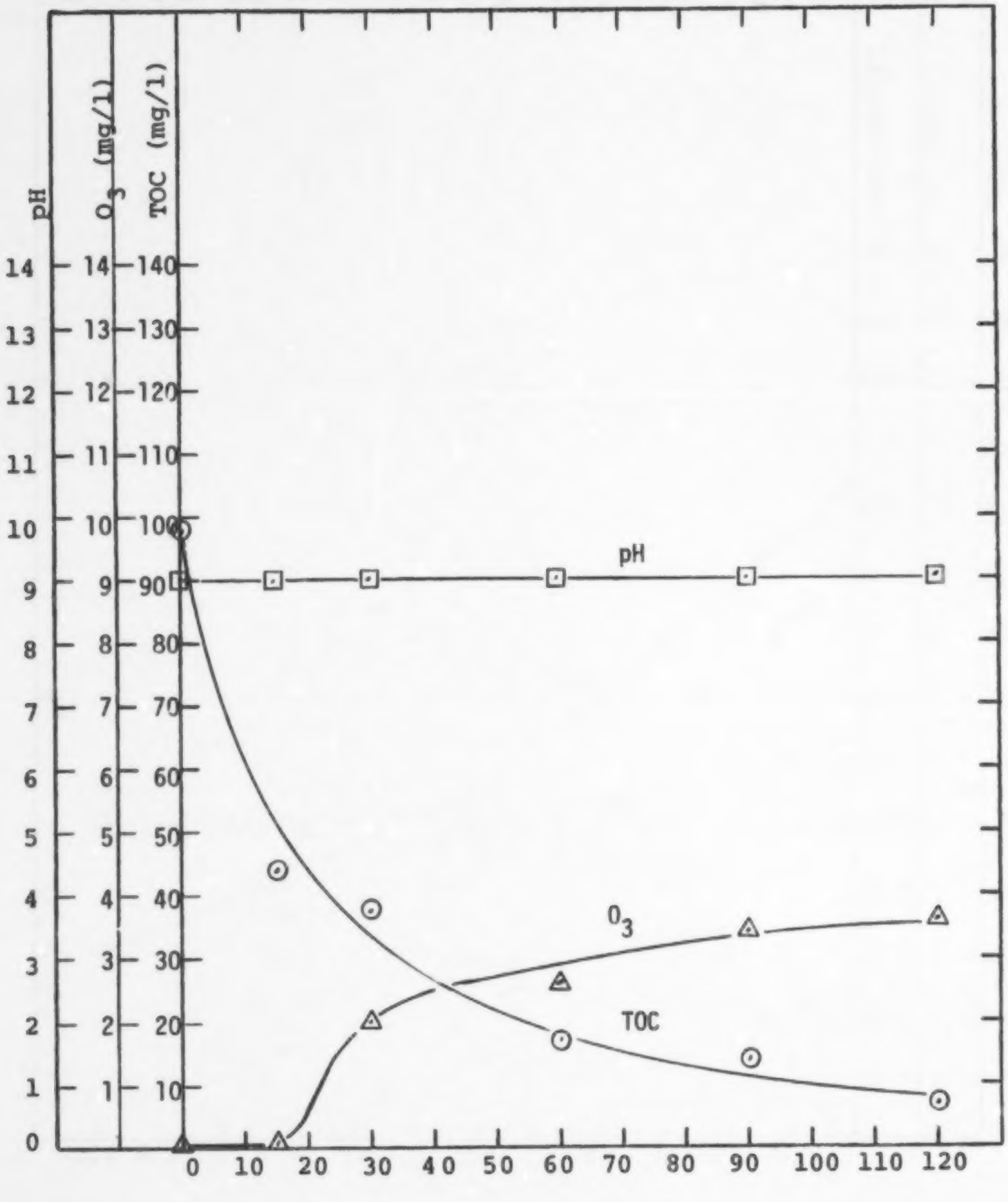

Figure A-8. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 9 without UV light.

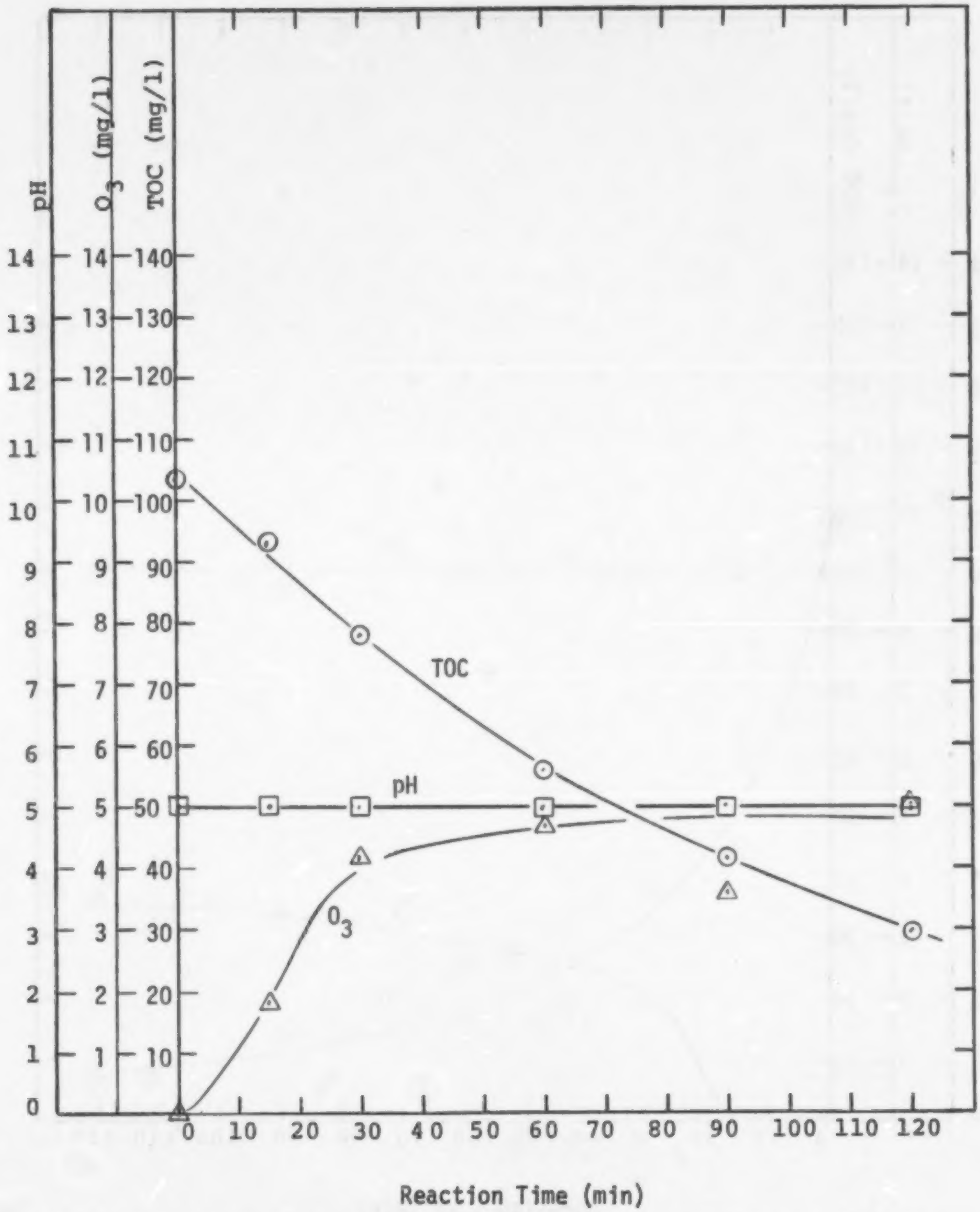

Figure A-9. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 5 with UV light.

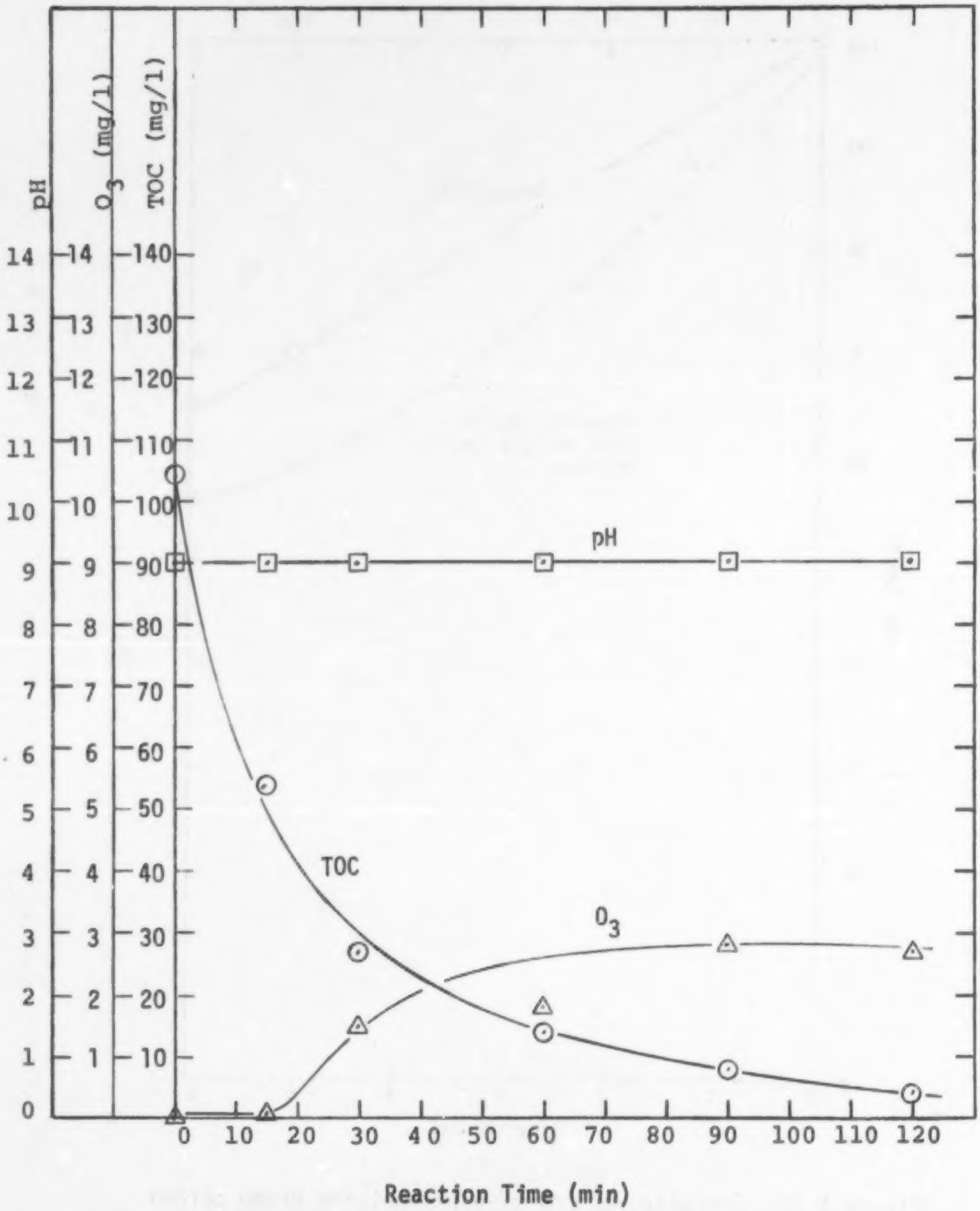

Figure A-10. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 9 with UV light.

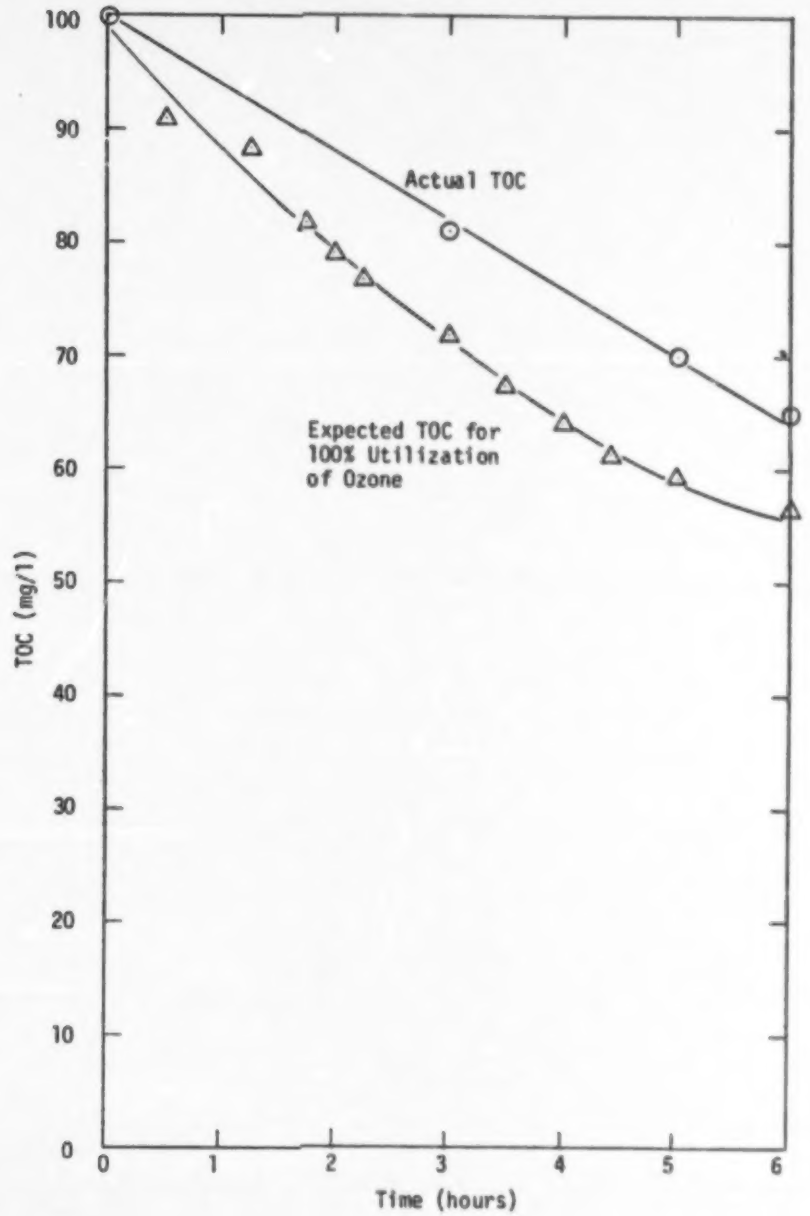

Figure A-11. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 5 without UV light (type B).

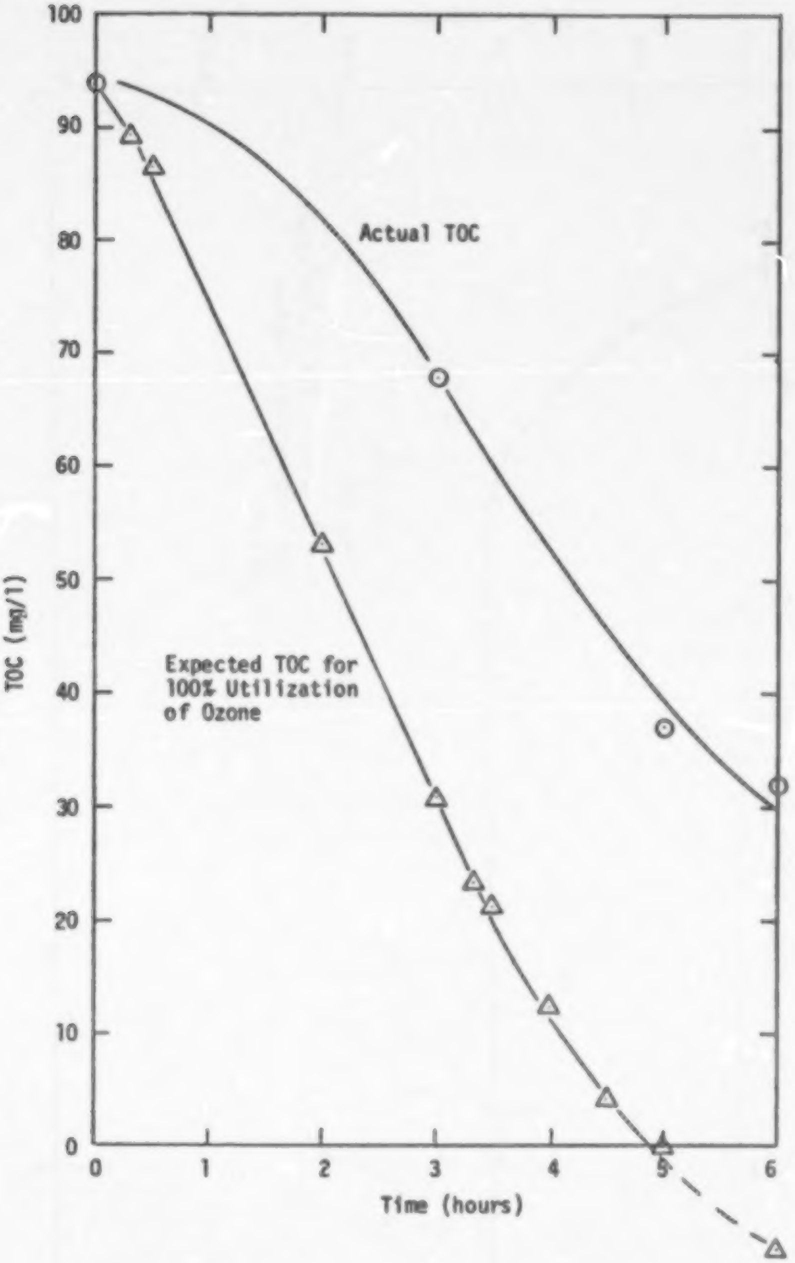

Figure A-12. Ozonation of end-of-pipe emulsion crumb carbon effluent at 30°C and pH 9 without UV light (type B).

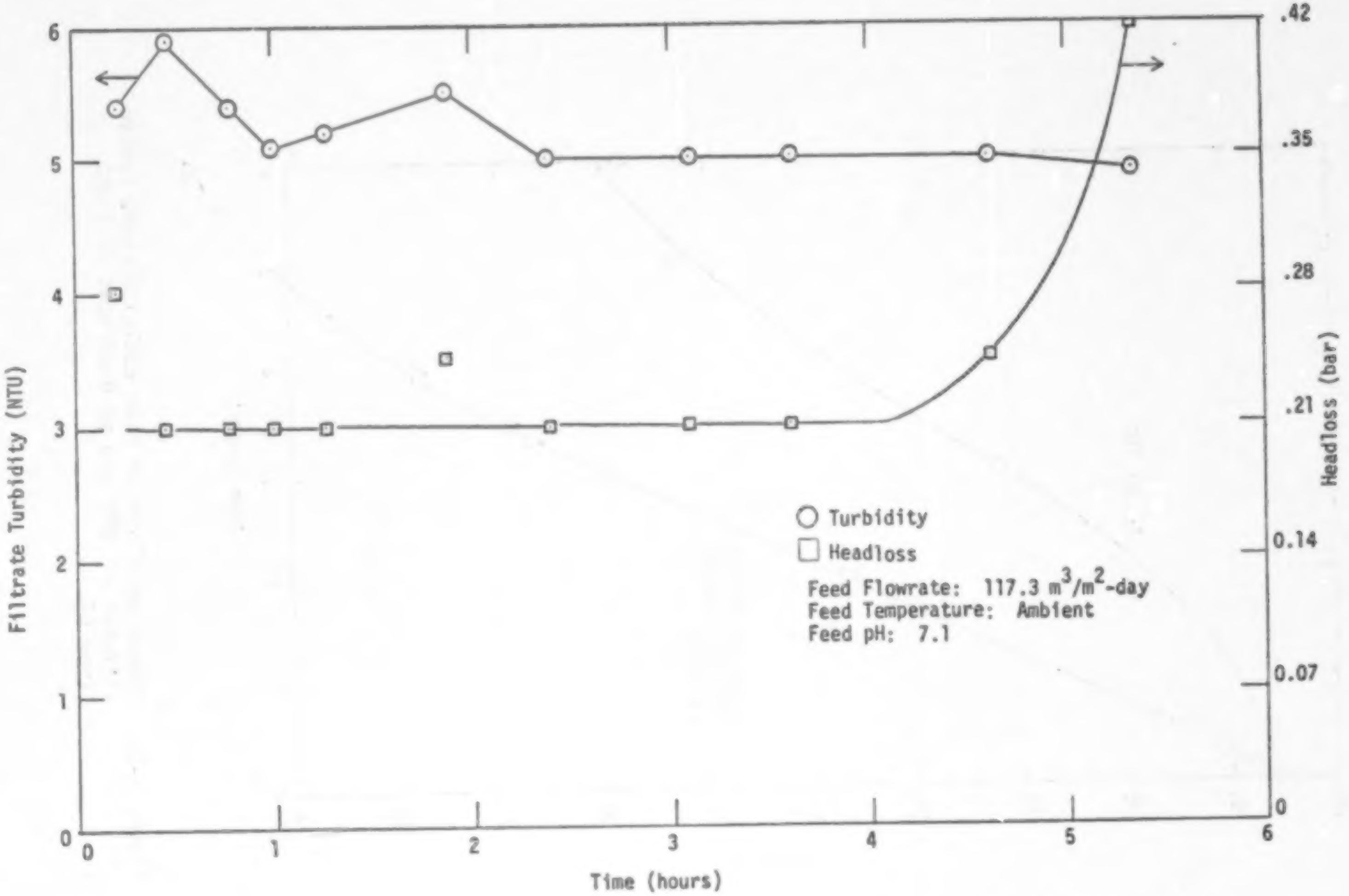

Figure A-13. Filtrate turbidity and column headloss vs. time for dual-media depth filtration of secondary treated emulsion crumb wastewater; first processing period; 0.23 m diameter column.

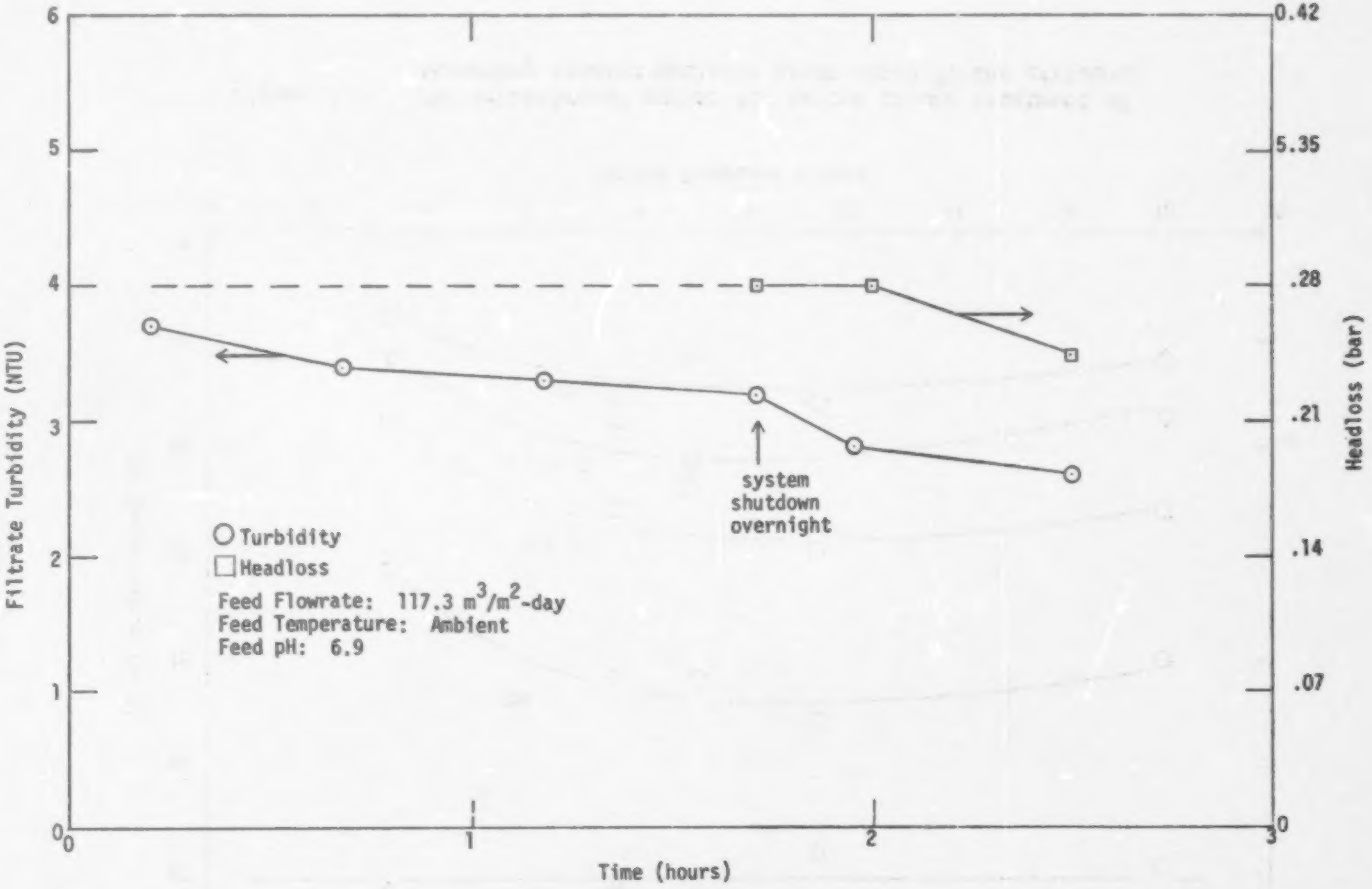

Figure A-14. Filtrate turbidity and column headloss vs. time for dual-media depth filtration of secondary treated emulsion crumb wastewater; second processing period; 0.23 m diameter column.

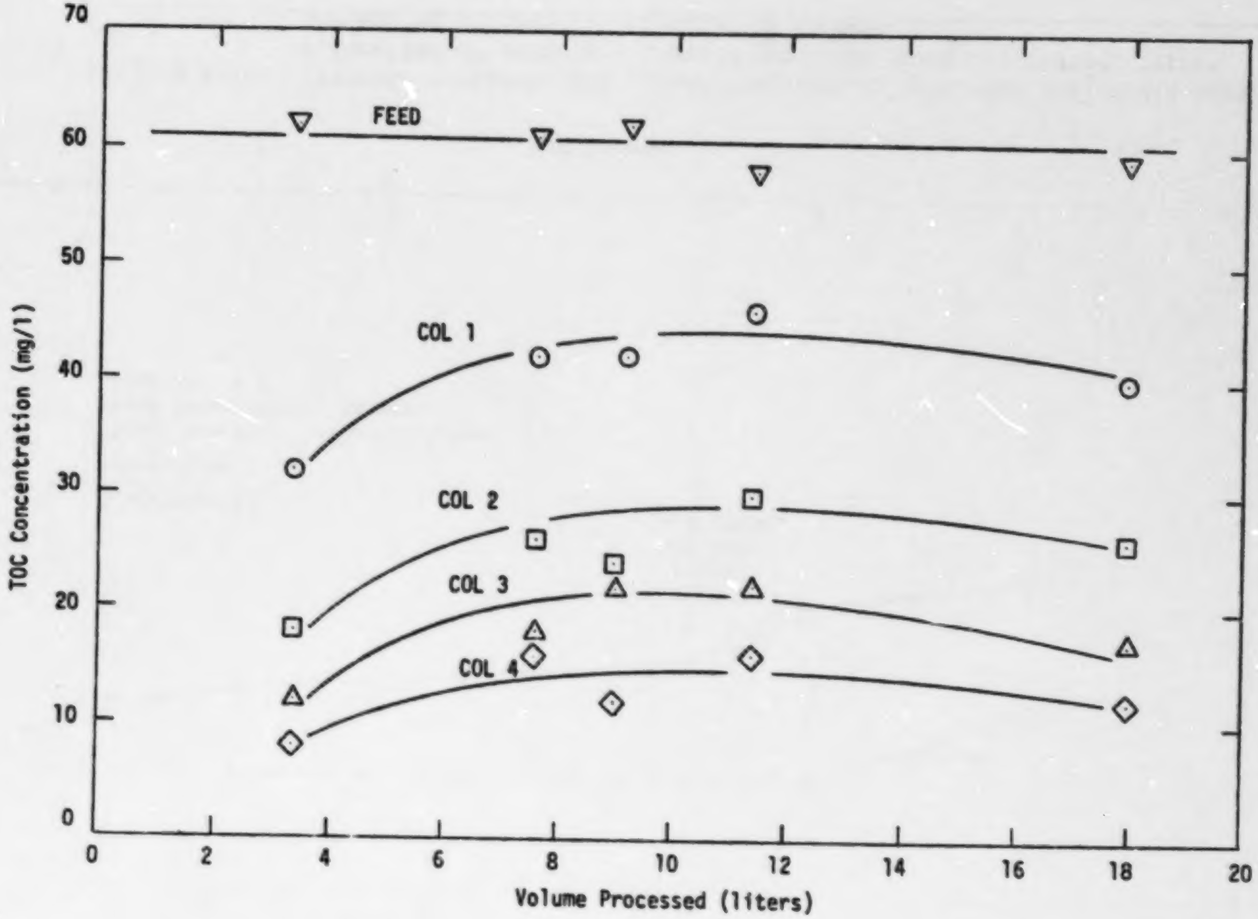

Figure A-15. TOC breakthrough curves for carbon column treatment of secondary treated emulsion crumb depth filter effluent.

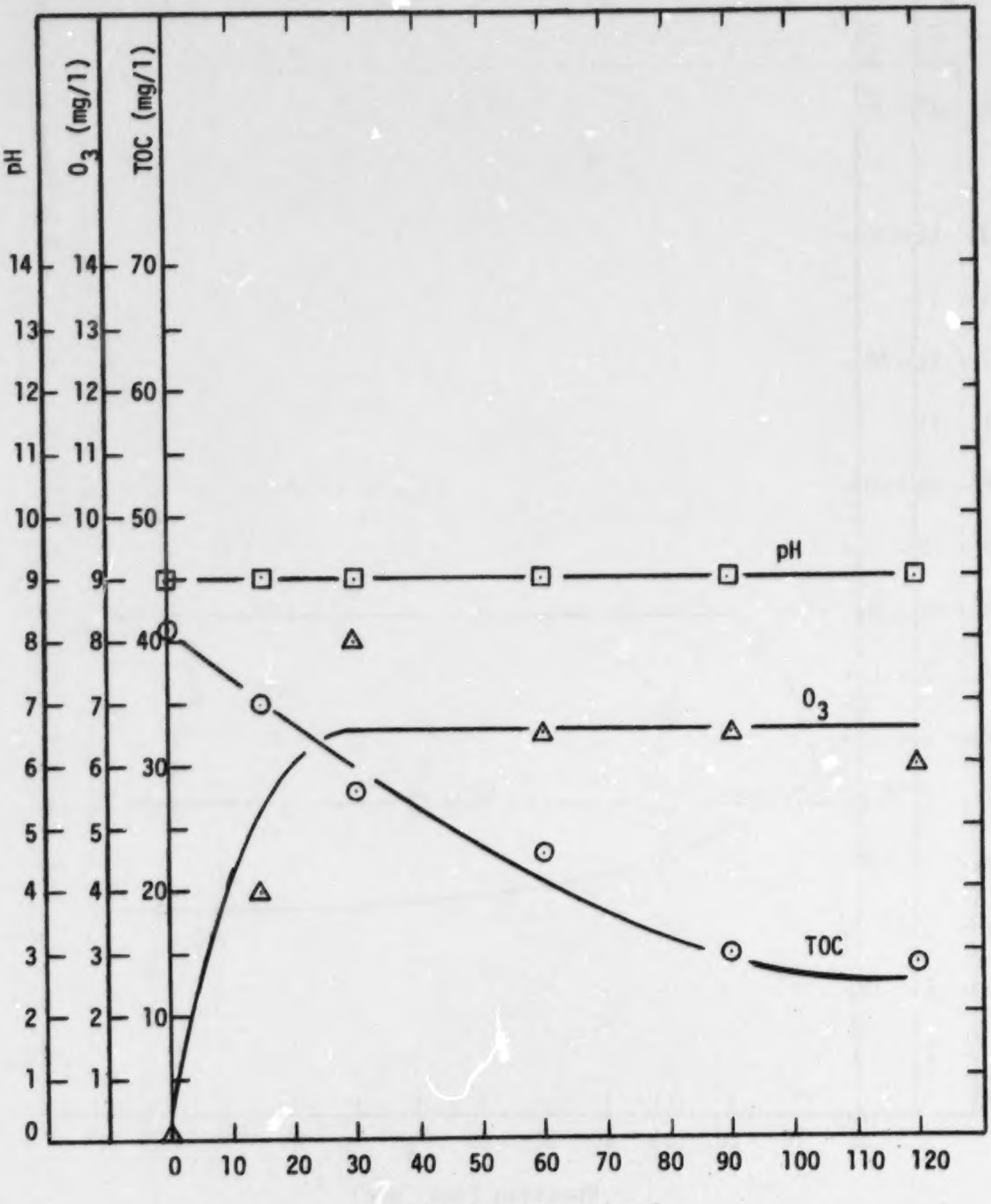

Figure B-1. Ozonation of end-of-pipe solution crumb carbon effluent at 30°C and pH 9 without UV light.

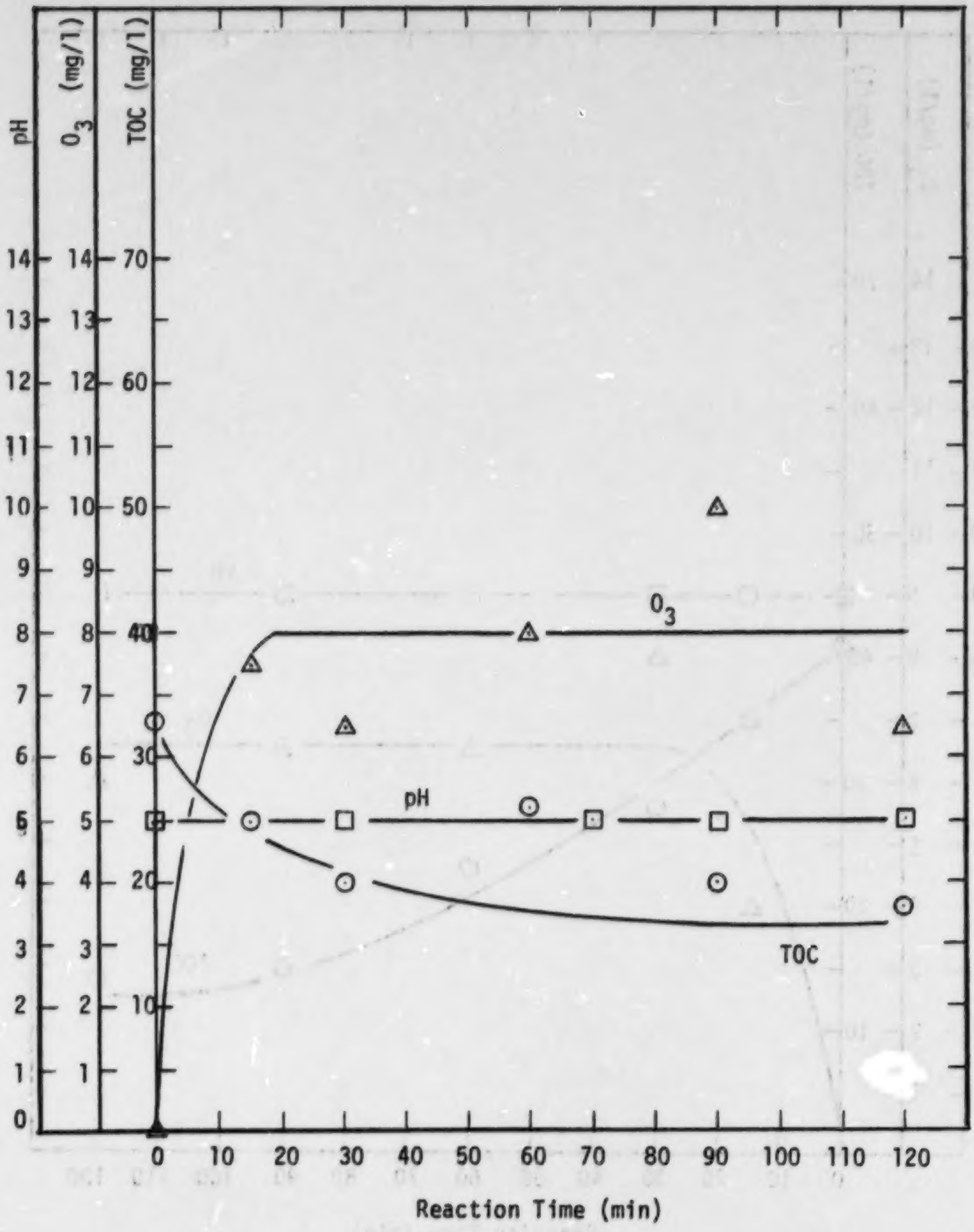

Figure B-2. Ozonation of end-of-pipe solution crumb carbon effluent at 30°C and pH 5 without UV light.

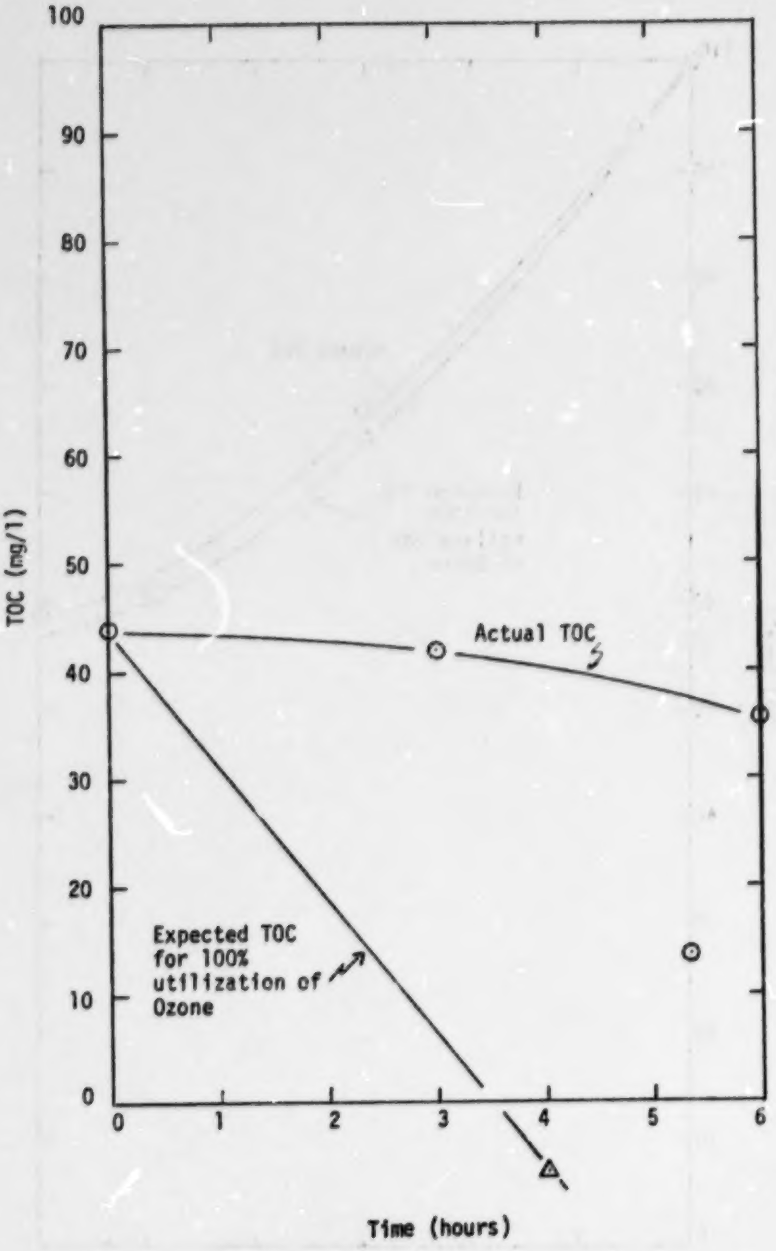

Figure B-3. Ozonation of end-of-pipe solution crumb carbon effluent at 30°C and pH 9 without UV light (type B).

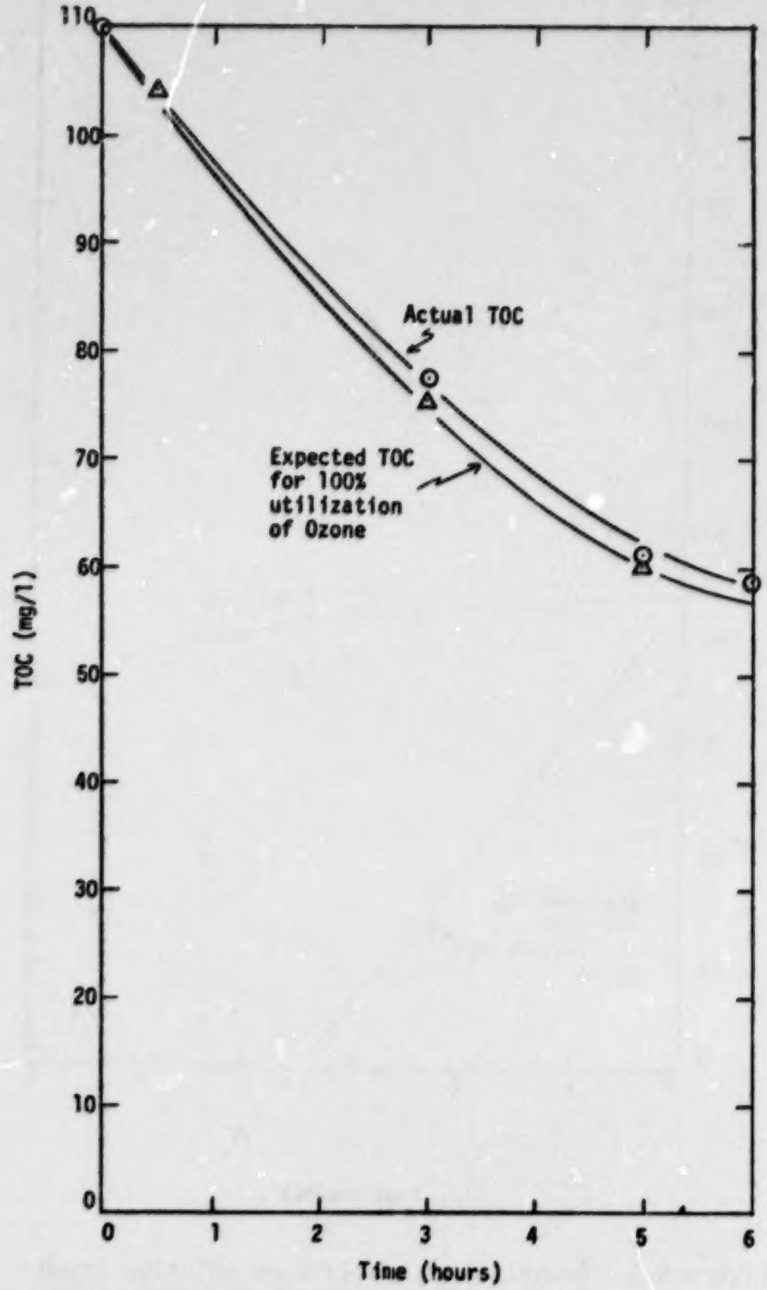

Figure B-4. Ozonation of end-of-pipe solution crumb carbon effluent at 30°C and pH 5 without UV light (type B).

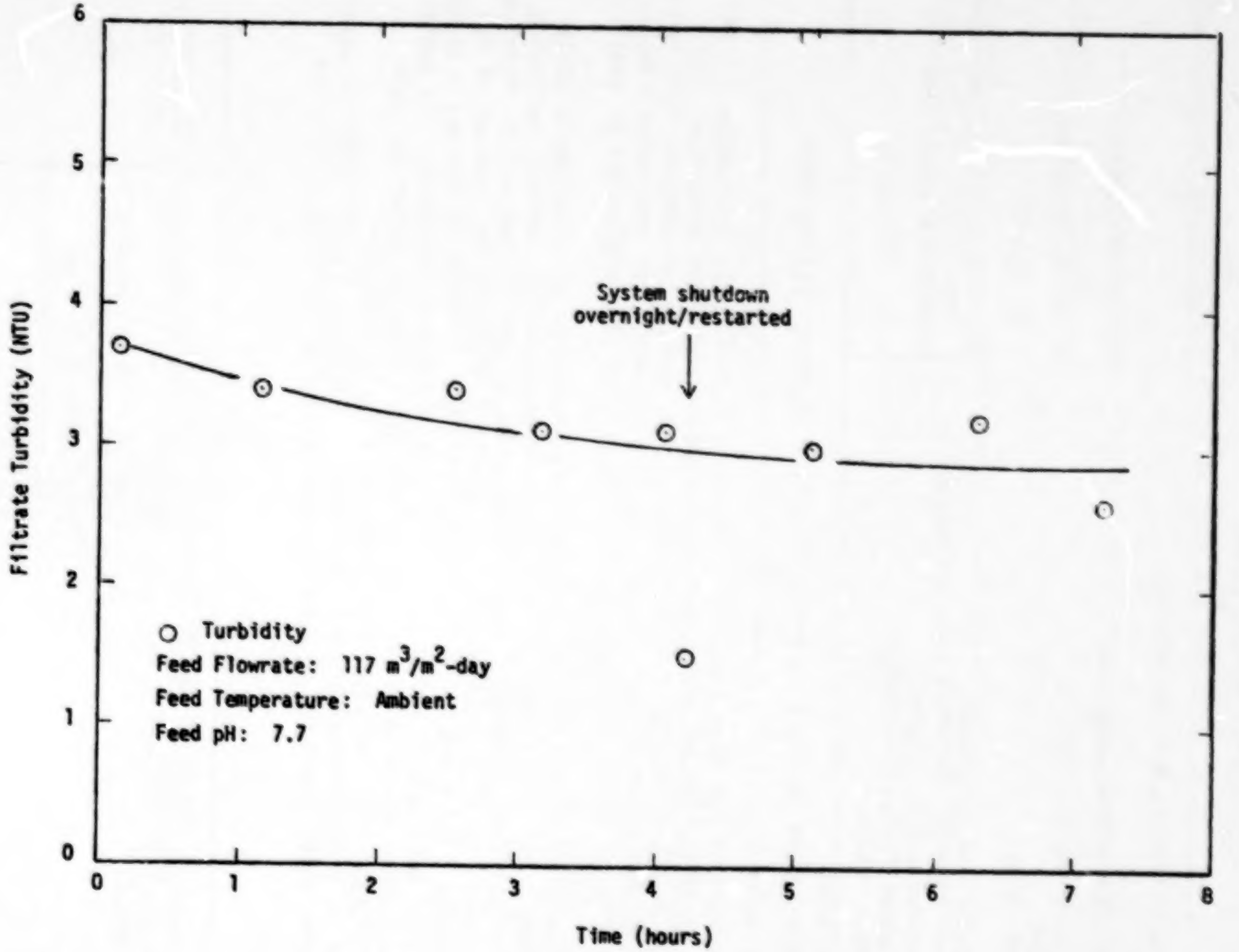

Figure B-5. Filtrate turbidity vs. time for dual-media depth filtration of secondary treated solution crumb wastewater; 0.23 m diameter column.